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An Investigation of the Preparation of High Molecular Weight  
Perfluorocarbon Polyethers

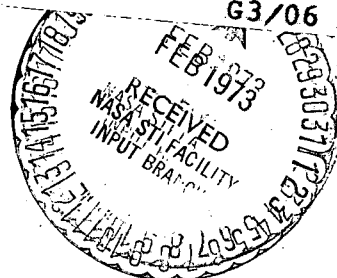
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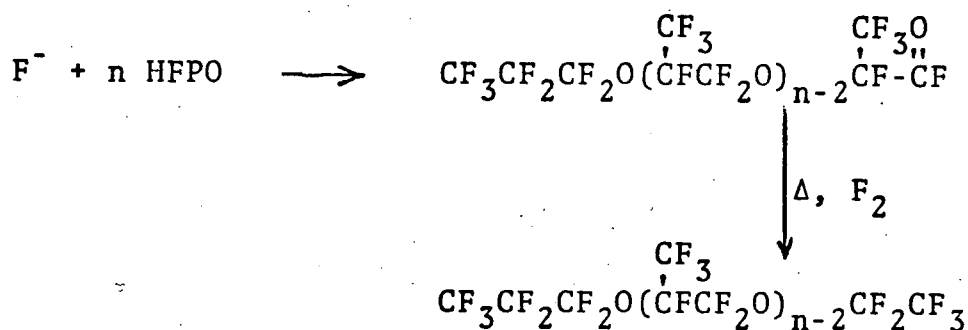


## Introduction

There is an important need for inert elastomers having good low temperature flexibility and high temperature stability. Viton A is used successfully at "high" temperatures but cannot be employed satisfactorily at temperatures much below  $-^{\circ}\text{C}$ . Fluorosilicone rubber has been developed with utility as low as  $-75^{\circ}$  but it is not a strong material relative to other materials and it cannot be satisfactorily employed at temperatures as high as might be desired. Nitro rubber also has its disadvantages, notably that it decomposes rapidly at temperatures above  $200^{\circ}\text{C}$ .

However, within recent years stable inert fluids have been made from hexafluoropropene oxide (HFPO) and these have been found to have unusually large liquid temperature ranges.

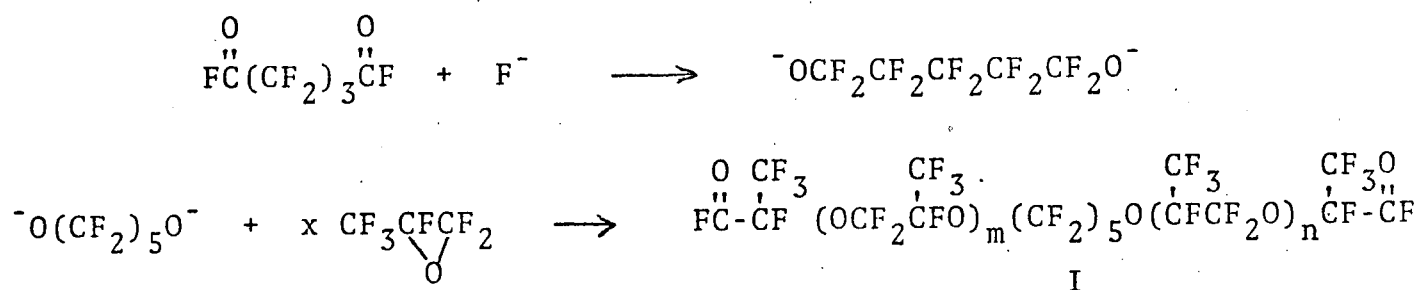
Although it is not particularly easy to prepare such compounds, they can be prepared in a two-step synthesis: 1) formation of the oligomer of HFPO and 2) the conversion of reactive fluoride end groups to an inert group such as an ether.



Values of  $n$  as high as 35 have been obtained but the molecular weight was not nearly high enough to give a gum. Probably a major cause of failure to form high molecular weight products by this

procedure has been the lack of compatibility of the fluoride initiator and the growing chain.

Another approach to oligomers of HFPO has been through the use of diacid fluorides such as perfluoroglutaric fluoride which of course, give long chain diacid fluorides.



In the present study, considerable attention was given to compounds of the type shown directly above since they contain polyether interiors with functional groups at each end and were theoretically capable of reaction with other bifunctional molecules to give polymers. Furthermore, hexafluoropropene oxide was available from the duPont Co. and no method for its synthesis had to be developed.

When this contract was initiated, two approaches to elastomers using compounds of type I seemed feasible. In the first the acid fluorides would be converted to alkyl diiodides and photolyzed to polymers. In the second, trifluorovinyl groups would be incorporated into the prepolymer chain and heated to give repeating cyclobutane structures. Neither of these routes produced any polymer.

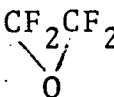
However, it was found that the acid fluoride end groups would react with fluorodienes to give elastomers which were insoluble in common reagents. The chemistry involved is described in the discussion section.

### Conclusions:

The initial objective of this contract has been realized, namely, the discovery of methods of formation of high molecular weight gums containing perfluorinated polyether groups in the backbone.

### Recommendations:

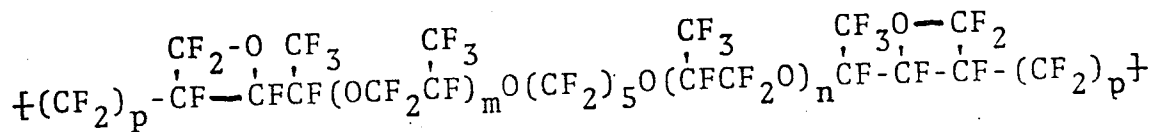
That research be continued in the area of the synthesis of high molecular weight gums containing perfluoroether linkages via the photolysis of carbonyl compounds and dienes. A study should be made of reaction conditions which lead to the best gums using model compounds. Furthermore, attention should be given to the use of other epoxides than HFPO, such as



$(\text{CF}_3)_2\text{C}-\text{C}(\text{CF}_3)_2$  which might give elastomers with extreme thermal stability.

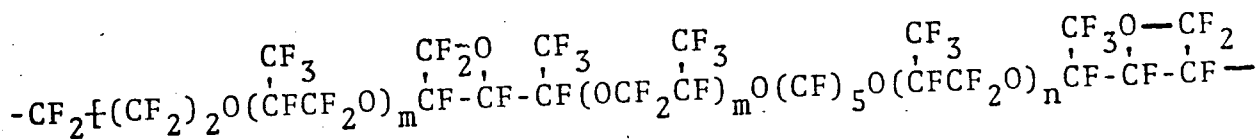
## Abstract

High molecular weight perfluorocarbon polyether gums have been obtained by photolysis of perfluorodienes and diacyl fluorides containing a perfluorocarbon polyether backbond. The materials obtained can be represented;

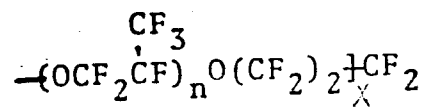


$m + n = 4, 5, 6$  or  $7$ ;  $p = 0, 1$  or  $2$ .

and by;



$m + n = 4, 5, 6$  or  $7$ .



A method has been developed whereby reactive acyl fluoride and trifluorovinyl end groups are converted into inert structures.

In order to investigate the possible preparation of difunctional molecules which may be useful in polymer synthesis, the reactions of hexafluoropropene oxide (HFPO) with Grignard and organolithium reagents have been studied.

Reactions of various nucleophilic reagents with HFPO have also been investigated.

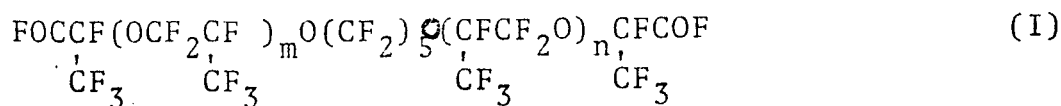
## Discussion

### Formation of High Molecular Weight Materials

High molecular weight perfluorocarbon polyethers have been obtained.

These materials were prepared by photolysis of diacylfluorides

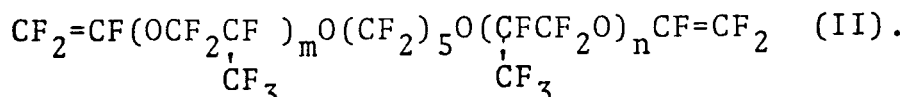
of the type (I),



$m + n = 4, 6$ -EDAF:  $m + n = 5, 7$ -EDAF:  $m + n = 6, 8$ -EDAF  $m + n = 7, 9$ -EDAF.

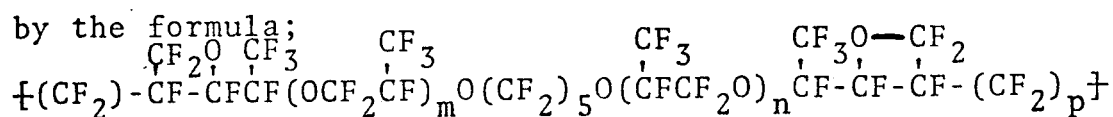
together with perfluorodienes of the type  $\text{CF}_2=\text{CF}=\text{CF}_2$ ,

$\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}=\text{CF}_2$ ,  $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{CF}=\text{CF}_2$  and



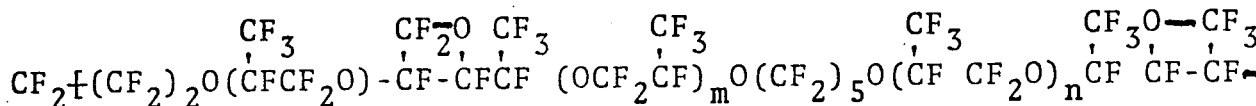
( $m + n = 4, 5, 6$  or  $7$ ).

The high molecular weight perfluorocarbon polyether is represented

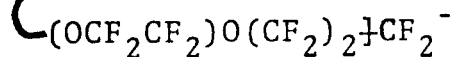


$m + n = 4, 5, 6$  or  $7$ ;  $p = 0, 1$  or  $2$ .

or in the case of the diene (II) by the formula



$m + n = 4, 5, 6$  or  $7$ .

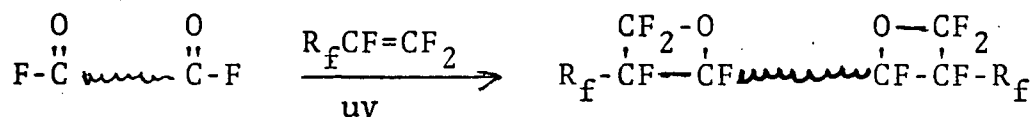


Preparation of acyl fluorides of the type (I) (EDAF's) was carried out by addition of HFPO to perfluoroglutaryl fluoride in diglyme in presence of a small amount of Caesium fluoride. After reaction and removal of diglyme, distillation under high vacuum gave EDAF's 6-9 in good yield. The perfluorodiene (II) was obtained by pyrolysis of the dipotassium salt of EDAF's at  $230-240^\circ$ , and purified by distillation at reduced pressure.

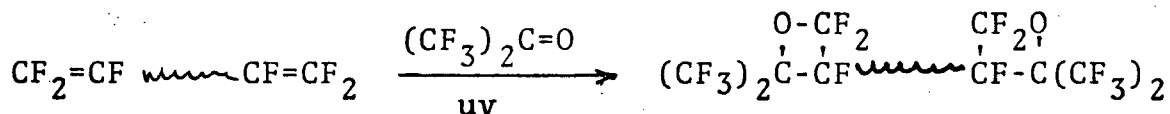
The high molecular weight material contains oxetane ring linkages formed, under photolytic conditions between the  $\text{CF}=\text{O}$  and

$\text{CF}_2=\text{CF}$  groupings. The use of diacyl fluorides and perfluorodiolefins thus forms a linear polymer via oxetane ring linkages.

Since the end groups of the perfluorocarbon polyether are reactive acyl fluoride or trifluorovinyl groups, a novel procedure for conversion of these groups into inert structures has been employed. Material containing reactive acyl fluoride and/or trifluorovinyl end groups is photolysed first with a perfluoroolefin e.g., hexafluoropropene or perfluoro-1-heptene to form the inert oxetane ring structure;



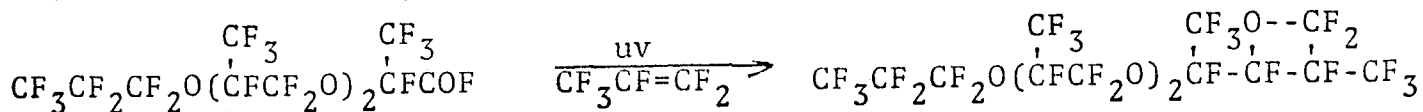
After removal of unreacted perfluoroolefin, the material was photolysed in the presence of hexafluoroacetone which converts any trifluorovinyl groups to the inert oxetane ring structure;



It is possible that if perfluoroketones are prepared from the EDAF acyl fluorides (eg. via the ester and its reaction with perfluorodienes will yield high molecular weight perfluorocarbonpolyethers none readily thru using the EDAF compounds themselves. The formation of oxetanes by photolysis of perfluoroolefins with ketones is reported to take place more readily than with acyl fluorides.

A number of possible methods of cross-linking the materials have been under consideration and it is felt that a suitable cross-linking method could be found.

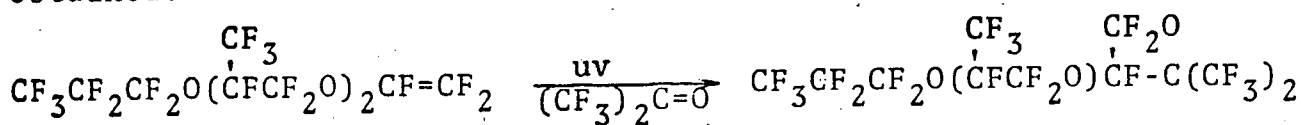
The formation of a stable fluid by end capping hexafluoropropene oxide tetramer by photolysis of this material with hexafluoropropene has been carried out;



Pyrolysis of the potassium salt of the above tetramer has led to the formation of the corresponding olefin;



Photolysis of this olefin with hexafluoroacetone has been carried out and the material containing an oxetane ring has been obtained:



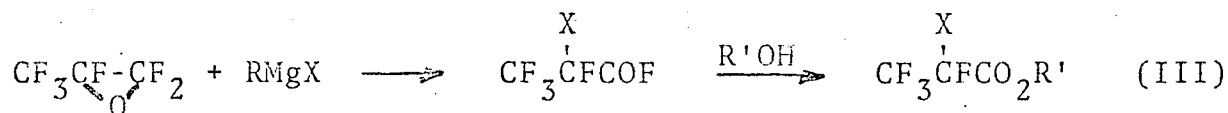
An investigation of the reaction of 7-EDAF with pentafluoropyridene in diglyme in the presence of fluoride ion did not yield any high molecular weight materials. It was hoped that fluoride ion catalysed reaction of EDAF with pentafluoropyridene at the 2,4 or 6 positions would take place to yield high molecular weight materials.

#### The Reaction of HFPO with Organometallic Reagents

The investigation of the reaction of HFPO with both Grignard and organolithium reagents commenced by previous workers has been concluded. It was hoped that these reactions would lead to potentially useful difunction molecules for polymer synthesis, e.g. the reaction of HFPO and  $\text{CF}_2=\text{CFMgBr}$ .

The treatment of HFPO with one equivalent of Grignard reagent yielded only compounds of the type (III) i.e.,



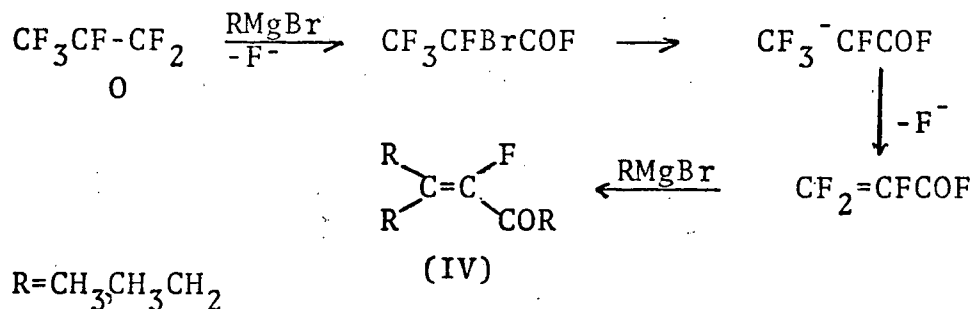


$\text{R}=\text{CH}_3, \text{CH}_3\text{CH}_2, \text{C}_6\text{H}_5, \text{CH}_2=\text{CHCH}_2, \text{CF}_2=\text{CF}$

$\text{X}=\text{Cl}$  or  $\text{Br}$

$\text{R}'=\text{CH}_3$  or  $\text{CH}_3\text{CH}_2$

It is considered that products of the type (III) are formed by halide ion attack upon HFPO, the source of halide ion being due to the equilibrium  $2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$ . When carried out reaction of HFPO and diethylmagnesium gave a low yield of a mixture of six components.



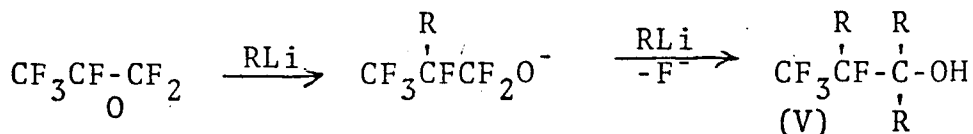
This possible route is supported by the experimental observations that treatment of  $\text{CF}_3\text{CFBrCOF}$  and  $\text{CF}_2=\text{CFCOF}$  with excess methylmagnesium bromide yield the ketone  $\text{Me}_2\text{C}=\text{CFCOMe}$ .

Treatment of the ester  $\text{CF}_2=\text{CFCO}_2\text{CH}_3$  with excess methylmagnesium bromide yielded the ketone  $\text{Me}_2\text{C}=\text{CFCOMe}$  which is in contrast to treatment of the ester  $\text{CF}_2=\text{CFCF}_2\text{CO}_2\text{CH}_3$  with excess methylmagnesium bromide which yielded the carbinol  $\text{CF}_2\text{BrCF}=\text{CFC}(\text{CH}_3)_2\text{OH}$ . Presumably the latter reaction takes place via attack of bromide ion on the terminal  $\text{CF}_2=$  group followed by double bond shift and loss of fluoride ion, and conversion of the ester function to the carbinol by reaction with Grignard reagent.

Reaction of HFPO with an excess of trifluorovinylmagnesium

bromide did not yield a ketone of the type  $(\text{CF}_2=\text{CF})_2\text{C}=\text{CFCOCF}=\text{CF}_2$ . It is probable that attack of Grignard reagents on  $\text{CF}_2=\text{CF}$  groups takes place readily to yield the high molecular weight tar obtained.

Reaction of alkyllithium reagents with HFPO yielded products of the type (V)



$\text{R}=\text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, \text{CH}_3(\text{CH}_2)_4$

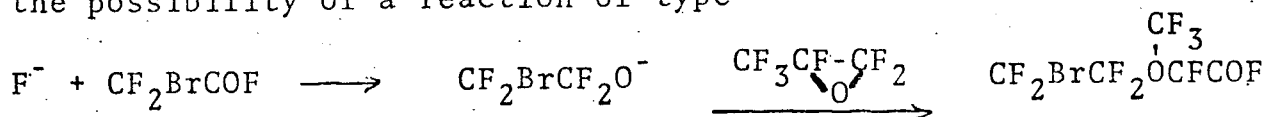
The reaction of equimolar amounts of methyllithium and HFPO yielded product (V) ( $\text{R}=\text{CH}_3$ ) in 28% yield indicating that initial attack of the alkyllithium reagent at the CF carbon is the difficult step of the reaction. Once this initial attack has taken place formation of the carbinol takes place readily. These reactions are consistent with the chemistry of HFPO since nucleophilic attack takes place at the most susceptible CF group. However, reaction of HFPO and n-butyllithium gives  $\text{CF}_3\text{C}(\text{OH})(\text{C}_4\text{H}_9)\text{CF}_2(\text{C}_4\text{H}_9)$  formed by attack at the terminal  $\text{CF}_2$  group. The different position of attack of n-butyllithium as compared to other alkyllithium reagents is difficult to explain.

Only tarry material was obtained from the reactions of trifluorovinyl lithium and 3,3,3-trifluoropropynyl lithium and HFPO. In these cases it is probable that decomposition of the lithium compound takes place at a temperature too low for the reaction with HFPO to occur. Products of these reactions, if obtained, may have been useful in polymer synthesis.

#### Reaction of HFPO with nucleophiles

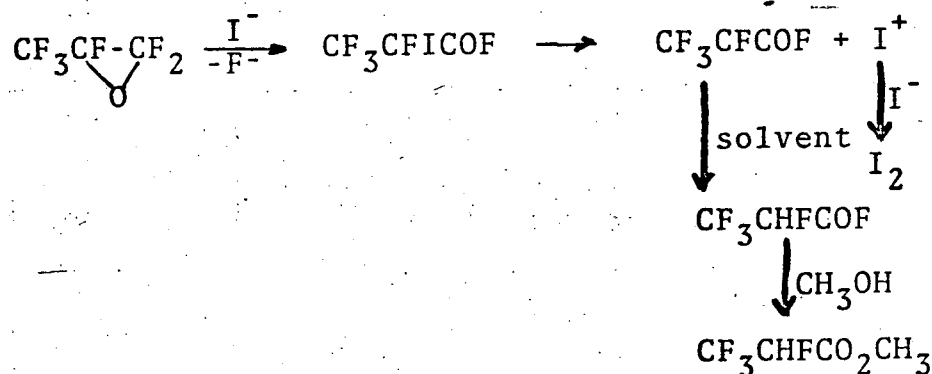
The acyl fluoride  $\text{CF}_2\text{BrCOF}$  was prepared and its reaction with fluoride ion and the HFPO was carried out in order to investigate

the possibility of a reaction of type

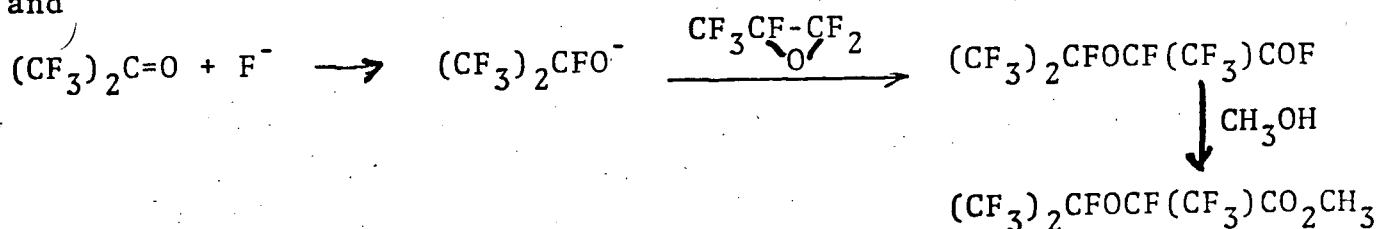


However the product  $\text{CF}_3\text{CF}_2\text{CO}_2\text{CH}_3$  was isolated from the reaction (addition of methanol during work-up) indication that fluoride ion reacts preferentially with HFPO and not with the acyl fluoride  $\text{CF}_2\text{BrCOF}$ .

The reaction of hexafluoroacetone, iodide ion and HFPO was also studied, in this case the major product isolated was  $(\text{CF}_3)_2\text{CFOCF}(\text{CF}_3)\text{CO}_2\text{CH}_3$ , a small amount of the ester  $\text{CF}_3\text{CHFCO}_2\text{Me}$  was also isolated. This reaction thus takes place in the following way;



and



The reaction of carbonyl fluoride, iodide ion and HFPO yielded a complex mixture of products with no single component predominating.

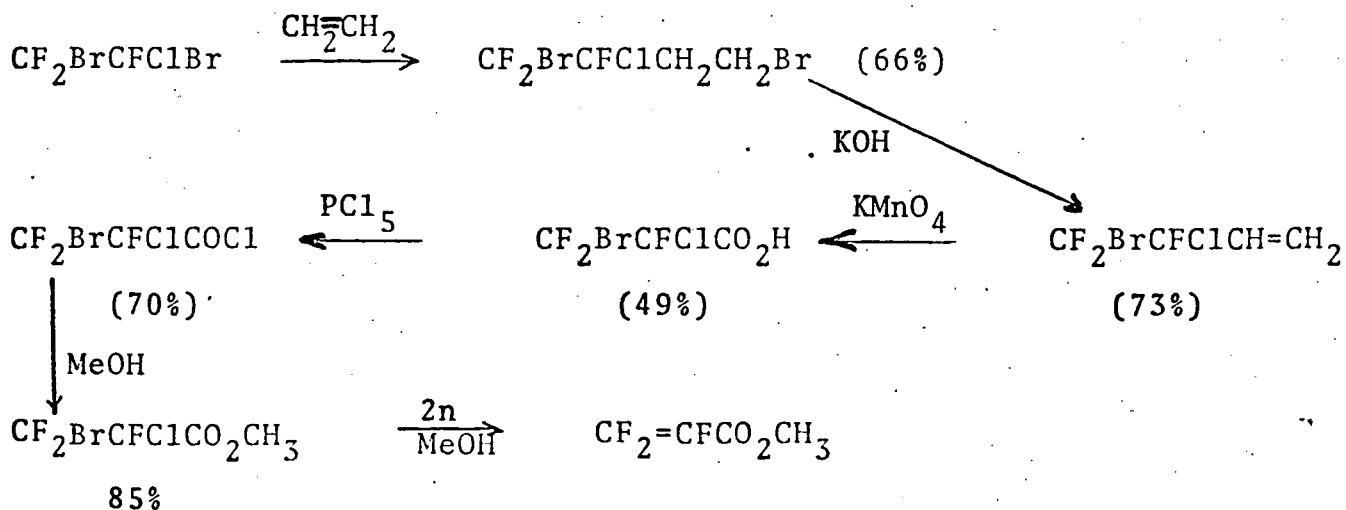
A study of the reactions of HFPO and cyanide ion was carried out, when carried out using potassium cyanide in both dimethylformamide and diglyme, only tar was obtained. A study of the reaction of zinc cyanide and HFPO has also been made on the basis

that zinc fluoride is insoluble in the solvent used (diglyme), and this would help to prevent interference by reaction of fluoride ion with HFPO. A mixture of two compounds was obtained from this reaction, these could not definitely be identified. Reaction of silver cyanide (AgCN) with HFPO gave a small amount of a mixture which was shown by glc to consist of eight components, these were not separated.

Reaction of calcium carbide and HFPO in diglyme or tetraglyme yielded the ester  $\text{CF}_3\text{CF}(\text{OCH}_3)\text{CO}_2\text{CH}_3$  (ca. 50%). This ester is probably formed by reaction of the diglyme or tetraglyme solvent with HFPO.

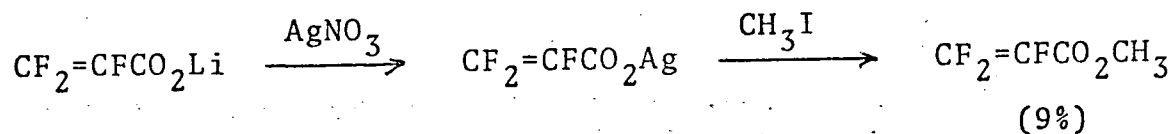
The reaction of lithium acetylide (in the form of the ethylene diamine complex  $\text{LiC}\equiv\text{CHH}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  with HFPO in diglyme yielded only a small amount of tarry material. Treatment of HFPO with sodium acetylide in THF in the presence of hexamethylphosphorous triamide resulted in an explosion. When repeated without hexamethylphosphorous triamide being present, the reaction yielded only a viscous tar.

Numerous methods were investigated for the preparation of perfluoroacryoyl fluoride and the ester  $\text{CF}_2=\text{CF}\text{CO}_2\text{CH}_3$ . Initially the following route was used:

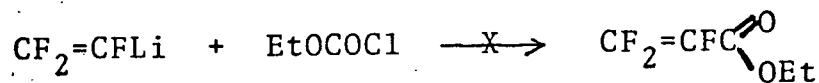
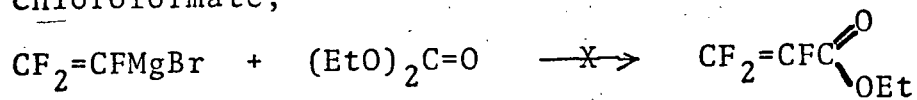


During reaction of  $\text{CF}_2\text{Br CFCl CO}_2\text{CH}_3$  and zinc in methanol explosion occurred, the reason for which is not apparent.

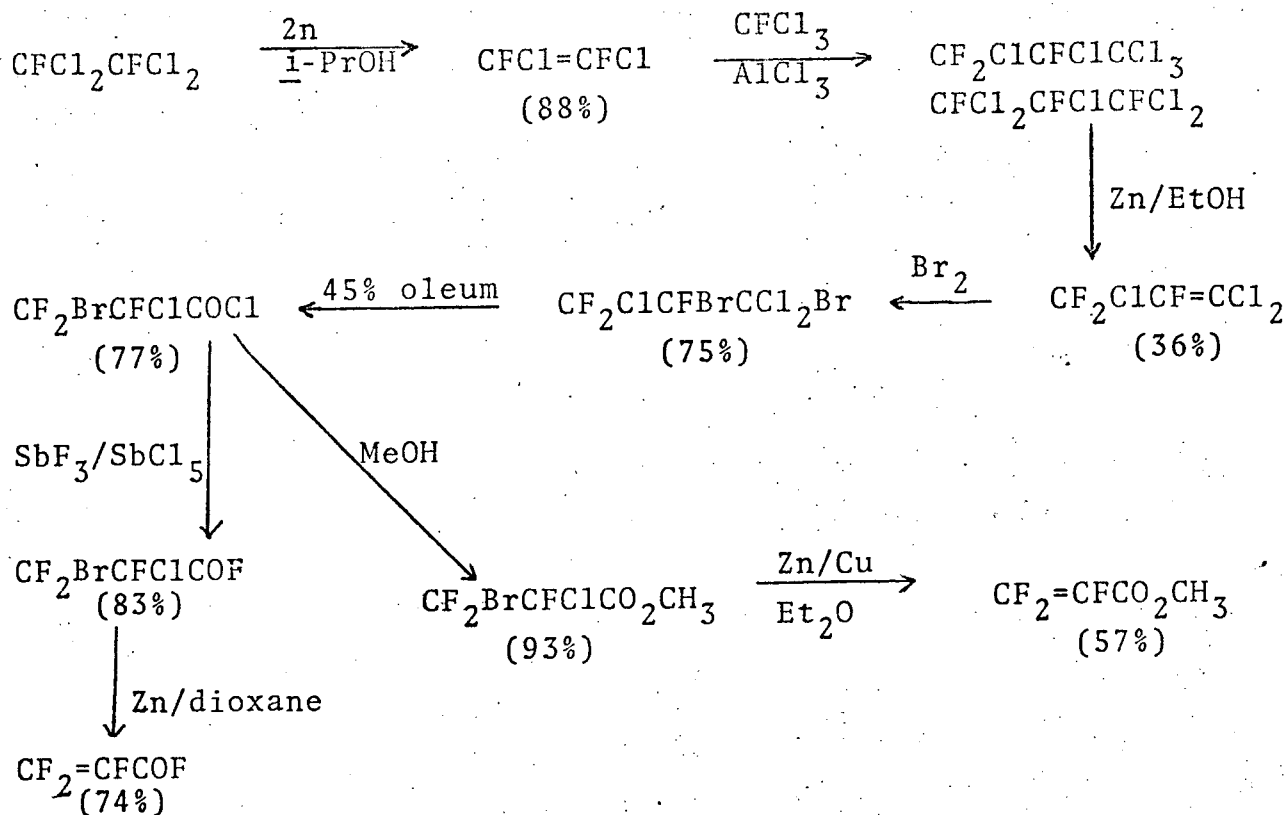
Formation of the salt  $\text{CF}_2=\text{CFCO}_2\text{Li}$  via carbonation of trifluorovinyl lithium was readily carried out and numerous attempts were made to convert this salt, and the acid  $\text{CF}_2=\text{CFCO}_2\text{H}$  formed by simple hydrolysis of the lithium salt, into the acyl chloride, acyl fluoride, or ester, were made without success. This is likely to be due to the susceptibility of the trifluorovinyl grouping to attack by reagents used. A low yield of the ester  $\text{CF}_2=\text{CFCO}_2\text{CH}_3$  was obtained in the following way;



Reaction of trifluorovinylmagnesium bromide with diethyl carbonate did not yield any characterisable products. Attempted reaction of trifluorovinyl lithium and ethyl chloroformate yielded only ethyl chloroformate;

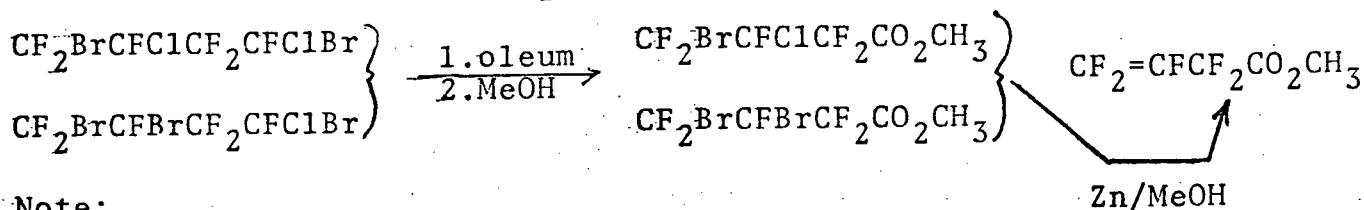


A satisfactory method which was used for the preparation of  $\text{CF}_2=\text{CFCOF}$  and the ester  $\text{CF}_2=\text{CFCO}_2\text{CH}_3$  was as follows;



Although a fairly long synthesis each step was found to be reliable and the yields reproducible.

The ester  $\text{CF}_2=\text{CFCF}_2\text{CO}_2\text{CH}_3$  was readily prepared from 2:1 telomer from reaction of  $\text{CF}_2=\text{CFBr}$  and  $\text{SOCl}_2$ , i.e.,



Note:

Reaction of excess n-butyllithium with HFPO in a 1:1 mixture of hexane/ether at 50-55° (24 hrs) was found to yield the carbinol  $\text{CF}_3\text{CF}(\text{C}_4\text{H}_9)\text{C}(\text{C}_4\text{H}_9)_2\text{OH}$  (55% yield). This product must be formed by attack of the alkyllithium reagent initially at the CF group of HFPO, as in the case of the reaction of other alkyllithium reagents studied. Previous workers on this contract have found that reaction of equimolar amounts of n-butyllithium in hexane and HFPO gives the carbinol  $\text{CF}_3\text{C}(\text{OH})(\text{C}_4\text{H}_9)\text{CF}_2(\text{C}_4\text{H}_9)$  (31%) which must be formed by initial attack of the alkyllithium reagent at the  $\text{CF}_2$  group of HFPO.

## Experimental

### Preparation of Hexafluoropropene (HFP)

A suspension of zinc (98 g., 1.5 moles) in 400 ml of 2-propanol was heated to reflux and 1,2-dibromohexafluoropropane (436 g., 1.5 moles) was added slowly. HFP, b.p.  $-29.4^{\circ}$ , was collected in a trap cooled to  $-76^{\circ}$ . Yield 95%.

### Preparation of Hexafluoropropene Epoxide (HFPO)

Methanol (1350 ml, techn. grade) was added to a 3-liter, 3-necked flask, equipped with stirrer, Dry-Ice/acetone condenser and thermometer. Potassium hydroxide (113.4 g., 2.02 moles) was dissolved in water (178 ml) and added to the alcohol. The flask was cooled to  $-45$  to  $-50^{\circ}$  and hydrogen peroxide (50% 675 ml.) was added slowly, the temperature being maintained at or below  $-45^{\circ}$ . Hexafluoropropene (135 g., 0.81 moles) was added rapidly to the flask in one portion as a liquid and stirred one hour at  $-45^{\circ}$ . The flask and the bath were allowed to warm until the mixture refluxed violently at  $-20^{\circ}$  to  $-24^{\circ}$  for about 10 minutes. The mixture was cooled to  $-40^{\circ}$  again for a few minutes, the reflux condenser was exchanged for a gas outlet tube and the temperature was slowly raised. The product was collected in traps, cooled to  $-76^{\circ}$ .

### Purification of HFPO

Crude HFPO containing unreacted HFP and  $\text{CO}_2$  was purified by passing the gas mixture through a solution of bromine (10 ml.) in 1,2-dibromohexafluoropropane (100 ml.). To remove bromine swept into the traps, the gas mixture was passed through a solution of sodium thiosulphate (5%, 100 ml.), and dried by passage through a drying tower containing anhydrous calcium sulphate. The carbon

dioxide was removed in vacuo. HFPO obtained (53.0 g., 0.32 mole, 40%) was identified by ir spectroscopy.

#### Reaction of HFPO and Methylmagnesium Bromide

Methylmagnesium Bromide was prepared by standard procedures by addition of bromo methane (19.0 g., 0.20 mole) to magnesium turnings (4.8 g., 0.2 g. atom) in dried THF. The solution of Grignard reagent was then cooled to 0° and HFPO (33.2 g., 0.20 mole) was bubbled into the solution. The mixture was stirred at room temperature (10 hrs) then cooled to -10° and methanol (20 ml.) added and stirred at room temperature. After washing with ice/water/HCl the organic material was extracted with ether, the ether extract was dried (CaSO<sub>4</sub>) and ether removed by distillation. Fractional distillation of the remaining material yielded CF<sub>3</sub>CFBrCO<sub>2</sub>CH<sub>3</sub> (31.0 g., 0.13 mole, 65%), b.p. 104-105°.

Anal. Calcd. for C<sub>4</sub>H<sub>3</sub>BrF<sub>4</sub>O<sub>2</sub>: C, 20.1; H, 1.25; F, 31.8.

Found: C, 20.2; H, 1.24; F, 31.8.

<sup>1</sup>H nmr singlet 5.68τ; <sup>19</sup>F nmr; doublet +0.56 ppm (CF<sub>3</sub>, J=9.0 Hz) and quartet +57.2 ppm (CFBr, J=9.0 Hz) (TFA ref.). Ir and mass spectrometry were consistent with the proposed structure.

#### Attempted reaction of methylmagnesium iodide and hexafluoropropene oxide

Methylmagnesium iodide was prepared in the usual way by the addition of iodomethane (21.4 g, 0.15 mole) to magnesium turnings (3.6 g, 0.15 g atom) in ether (150 ml). The Grignard reagent was placed in an autoclave which was then sealed and cooled to -196°. Hexafluoropropene oxide (24.9 g., 0.15 mole) was condensed into the autoclave which was then warmed to 40° and maintained at this



temperature (16 hrs.). The autoclave was opened and the contents taken in vacuo into another flask cooled to  $-196^{\circ}$ . The material remaining in the autoclave was seen to consist of mainly tarry material, idoine, a small amount of unreacted Grignard. Vacuum distillation of the material taken from the autoclave in vacuo resulted in decomposition of the material was the liberation of iodine.

#### Reaction of excess methyl magnesium bromide and hexafluoropropene oxide

Methyl magnesium bromide was prepared in the usual way by the addition of bromomethane (76.0 g., 0.80 mole) to magnesium turnings (20.0 g., 0.80 g. atom) in dried ether (250 ml). The solution of Grignard reagent was cooled to  $-5^{\circ}$  and hexafluoropropene oxide (33.2 g., 0.20 mole) was bubbled in over 1 1/2 hours. The reaction mixture was stirred at  $-5^{\circ}$  to  $0^{\circ}$  (1 hr), room temperature (10 hrs), ethanol (20 ml) was added and the reaction mixture was poured into ice/water-conc. HCl. The organic layer was separated, dried ( $\text{CaSO}_4$ ) and the ether removed by distillation. Fractional distillation of the remaining material yielded  $\text{Me}_2\text{C}=\text{CFCOMe}$  (11.2 g., 0.96 mole, 48%) identified by nmr and ir spectroscopy, b.p.  $67-68^{\circ}$  at 15 mm Hg.

Anal. Calcd for  $\text{C}_6\text{H}_9\text{FO}$ : C, 62.05; H, 7.76; F, 66.4.

Found: C, 62.14; H, 7.81; F, 66.2.

$^1\text{H}$  nmr indicated the presence of three distinct methyl groups at 7.91 $\tau$  (doublet,  $J=2.8$  Hz), 8.04 (doublet  $J=1.7$  Hz), and 8.20 $\tau$  (doublet,  $J=2.1$  Hz).  $^{19}\text{F}$  nmr showed a complex multiplet at 46.0 ppm (TFA ref.).

#### Reaction of excess Ethylmagnesium Bromide and Hexafluoropropane Oxide

Ethylmagnesium bromide was prepared by the addition of bromoethane (87.0 g., 0.80 mole) to magnesium turnings (19.2 g., 0.80

g. atom) in ether (400 ml). The solution of Grignard reagent was cooled to  $-20^{\circ}$  and hexafluoropropene oxide (33.2 g., 0.20 mole) was bubbled into the solution (2 hr). The reaction mixture was stirred at  $0^{\circ}$  (3 hr) then allowed to attain ambient temperature (4 hr). The reaction mixture was poured into ice-water/conc<sup>n</sup> HCl with care (some unreacted Grignard reagent was present). The organic material was extracted in the ether layer which was washed with water then dried (CaI<sub>2</sub>). The ether was removed by rapid distillation, the remaining material was fractionally distilled using a vacuum jacketed Vigreux column to yield  $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{CFCOCH}_2\text{CH}_3$  bp  $69-71^{\circ}$  at 20 mm Hg. (17.4 g., 0.11 mole, 55%). This material was identified by nmr and ir spectroscopy.

#### Reaction of Trifluorovinylmagnesium Bromide and HFPO

Trifluorovinylmagnesium bromide was prepared by the addition of trifluorovinyl bromide (32.2 g., 0.20 mole) to magnesium turnings (4.8 g., 0.20 g. atom) in THF at crystal of iodine. HFPO (33.2 g., 0.20 mole) was bubbled into the Grignard solution at  $0 \rightarrow -10^{\circ}$ ; the reaction mixture was then stirred at room temperature (8 hrs) and methanol (20 ml) added. After washing with ice/water/conc<sup>n</sup> HCl the organic material was extracted with ether. After drying (CaSO<sub>4</sub>) and removal of ether, fractional distillation of 5. The remaining material yielded  $\text{CF}_3\text{CFBrCO}_2\text{CH}_3$  (30.0 g., with a known pure sample.

#### Attempted reaction of Excess Trifluorovinylmagnesium Bromide and HFPO

Trifluorovinylmagnesium bromide (0.8 mole) was prepared as described previously. HFPO (33.2 g., 0.20 mole) was bubbled into the solution of Grignard reagent at  $-10 \rightarrow -15^{\circ}$ . The reaction mixture

was stirred at room temperature (10 hr), then washed with ice/water/HCl. The organic material was extracted with ether, after drying and removal of ether only viscous tarry material remained which could not be distilled even at 0.1 mm Hg.

Reaction of Perfluoroacryoyl fluoride and Methylmagnesium Bromide

Methylmagnesium bromide (0.4 mole) was prepared in the usual way in ether, then cooled to  $-78^{\circ}$  and perfluoroacryoyl fluoride,  $\text{CF}_2=\text{CFCOF}$  (12-8 g., 0.10 mole) was added (1 hr.). After addition the reaction mixture was allowed to attain room temperature (3 hr.) then stirred (8 hr.). Methanol (20 ml.) was added with further stirring then the reaction mixture was washed with ice-water/HCl, the organic material was extracted with ether, the ether extract was dried, after of ether by distillation, fractional distillation of the remaining material yielded  $(\text{CH}_3)_2\text{C}=\text{CFCOCH}_3$  (4.7 g., 0.035 mole, 35%) which was identified by comparison with a known pure sample.

The reaction of  $\text{CF}_2=\text{CF CO}_2\text{Me}$  and methylmagnesium bromide

Methylmagnesium bromide was prepared in the usual way from bromomethane (27.6g., 0.29 mole) and magnesium (7.0g., 0.29 g. atom) in ether (200 ml.) the solution of Grignard reagent was cooled to  $-78^{\circ}$  and the ester  $\text{CF}_2=\text{CFCO}_2\text{Me}$  (10.0g., 0.071 mole) was added (1 hour) in ether (25 ml.). The reaction mixture was warmed to room temperature (3 hr.) and then poured into ice water/conc HCl. The ether layer was extracted, washed with water, and dried ( $\text{CaSO}_4$ ). The ether was removed by distillation, fractionation of the remaining material yielded  $\text{Me}_2\text{C}=\text{CFCOMe}$  (4.3g., 0.37 mole, 53%) which was identified by i.r. and n.m.r. spectroscopy.

The reaction of  $\text{CF}_3\text{CBrFCOF}$  and excess Methylmagnesium Bromide

Methylmagnesium bromide was prepared by the slow addition of bromomethane (28.5 g., 0.30 mole) in dry ether to magnesium turnings (7.2 g., 0.20 g. atom) in ether (100 ml.) at 0-10°.

$\text{CF}_3\text{CBrFCOF}$  (21.1g., 0.10 mole) was condensed into the solution of Grignard reagent (1 hr.) which was maintained at ca.-50°. The reaction mixture was stirred at -45° (2 hr.) then warmed to room temperature (1 1/2 hr.) and stirred at room temperature (12 hr.). Methanol (15 ml.) was added and some reaction took place, after this reaction had subsided, the reaction mixture was poured into ice-water/conc. HCl, the organic layer was separated, washed with water (3 x 100 ml) and dried ( $\text{MgSO}_4$ ). After removal of ether by rapid distillation, the vpc-trace of the product mixture indicated two major components, (ca. 80% total) and 4 minor components. The two major components were separated by preparative scale vpc and identified as  $\text{CF}_3\text{CBrFCO}_2\text{Me}$  (3.9 g., 0.016 mole, 16%) and  $\text{Me}_2\text{C}=\text{CFCOMe}$  (7.2 g., 0.062 mole, 62%).

The Reaction of HFPO and Diethylmagnesium- Ethylmagnesium

bromide was prepared by the addition of bromoethane (32.3 g., 0.296 mole) to magnesium turnings (7.1 g., 0.296 g. atom) in dry ether (120 ml). 1,4-dioxan (26.0 g., 0.296 mole,  $\text{LiAlH}_4$  dried) was added to the rapidly stirred Grignard reagent (4 hr.). The reaction mixture was stirred for a further 10 hours then filtered under nitrogen.

HFPO (21.0g., 0.126 mole) was bubbled into the ether solution of diethylmagnesium which was maintained at  $-78^{\circ}$  (1 hr.). The reaction mixture was warmed slowly to room temperature, (6 hr.). Methanol (20 ml) was added to the reaction mixture which was then poured into water. The ether layer was extracted and washed with water (2x100 ml) and dried ( $\text{MgSO}_4$ ). After removal of ether, 3.2 g. of oil remained which was shown by v.p.c. to consist of six major components.

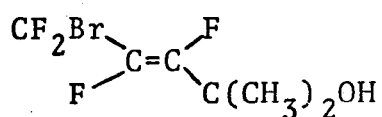
The Hydrolysis and Esterification of the Telomer Mixture

$\text{CClF}_2\text{.CBrF.CF}_2\text{.CBrClF}$  and  $\text{CBrF}_2\text{.CBrF.CF}_2\text{.CBrClF}$ .- The telomer mixture (500 g.) was placed in a flask fitted with condenser, dropping funnel and stirrer, 30% oleum (1000 g.) was added and the flask heated at  $100\text{--}120^{\circ}$  (3 days). Methanol (1000 ml., tech. grade) was added slowly (8 hr.) with rapid stirring. The mixture was then poured into ice/water and the organic material extracted and dried. V.p.c. indicated that the organic material consisted of the esters  $\text{CClF}_2\text{.CBrF.CF}_2\text{.CO}_2\text{Me}$  and  $\text{CBrF}_2\text{.CBrF.CF}_2\text{.CO}_2\text{Me}$  (440 g.) in the approx. ratio 3:1.

Dehalogenation of the Ester Mixture.- The mixture of  $\text{CClF}_2\text{.CBrF.CF}_2\text{.CO}_2\text{Me}$  and  $\text{CBrF}_2\text{.CBrF.CF}_2\text{CO}_2\text{Me}$  (440.0 g.) was added slowly (6 hr.) to zinc dust (196.0 g., 3.0 g. atoms) in refluxing methanol (950 ml.). Anhydrous zinc chloride (5.0 g.) was added to catalize the reaction. The reaction mixture was filtered and the ester was separated, washed with water (2x100 ml) and dried ( $\text{MgSO}_4$ ). Fractional distillation yielded  $\text{CF}_2\text{:CF.CF}_2\text{.CO}_2\text{Me}$  (130.0 g., 0.69 mole) b.p.  $95^{\circ}$

Reaction of  $\text{CF}_2:\text{CF}.\text{CF}_2.\text{CO}_2\text{Me}$  and Methylmagnesium Bromide.

Methylmagnesium bromide was prepared by the addition of bromomethane (76.0 g., 0.80 mole) to magnesium turnings (19.2 g., 0.8 g. atom) in ether (250 ml.). The ether solution of methyl magnesium bromide was added (3 hr.) to a stirred solution of  $\text{CF}_2:\text{CF}.\text{CF}_2.\text{CO}_2\text{Me}$  (38.0 g., 0.20 mole) in ether (100 ml.) maintained at ca.  $-30^\circ$ . The reaction mixture was allowed to attain room temperature slowly and then poured into ice/conc. HCl. The ether layer was separated, washed with water (3x100 ml.) then dried ( $\text{MgSO}_4$ ). After removal of ether, fractional distillation of the higher boiling material yielded a single fraction. An nmr investigation of this product showed it to be the carbinol



(22.5 g., 0.09 mole, 45%), bp  $71-72^\circ$  at 22 mm Hg.

Anal. Calcd. for  $\text{C}_6\text{H}_7\text{BrF}_4\text{O}$ : C, 28.7; H, 2.79; F, 30.25.

Found: C, 28.67; H, 2.65; F, 30.24.

$^1\text{H}$  nmr showed absorption a  $8.18\tau$  (triplet, 6H,  $J=2.0$  Hz) and  $5.04\tau$  (singlet, OH);  $^{19}\text{F}$  nmr (TFA ref.) showed absorption at  $-27.1$  ppm (doublet of doublets, 2F,  $J$  34.0 and 17.0 Hz),  $66.0$  ppm (doublet of triplets, 1F,  $J=134.0$  and 17.0 Hz). Infrared spectroscopy and mass spectrometry were consistent with the proposed structure.

Reaction of methyllithium and HFPO

Methyllithium (obtained from Foote Mineral Co.) (128 ml of 5% solution in ether=0.20 moles) was added slowly to HFPO (33.2 g., 0.20 mole) in ether at ca.  $10^\circ$ . HFPO was retained in the flask by use of a dry-ice/acetone condenser. An external trap cooled to  $-78^\circ$  was connected to the reaction flask and the reaction

stirred at room temperature (8 hr.). Ethanol (20 ml.) was then added and the reaction mixture poured onto ice/water -conc<sup>n</sup> HCl, the ether layer was extracted, dried (CaCl<sub>2</sub>) and the ether removed by distillation. Fractional distillation of the remaining material yielded the carbinol CF<sub>3</sub>CF(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>2</sub>OH (9.75 g., 0.056 mole, 28%). Material condensed in the -78° external trap was identified as unreacted HFPO (23.8 g., 0.14 mole, 70% recovered). <sup>1</sup>H nmr spectrum of the carbinol CF<sub>3</sub>CF(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>2</sub>OH showed absorption due to one distinct and two identical methyl groups and OH. The <sup>19</sup>F nmr showed absorption due to CF<sub>3</sub> with adjacent CF grouping.

Anal. calcd. for C<sub>6</sub>H<sub>10</sub>F<sub>40</sub>: C, 41.4; H, 5.75; F, 43.7.

Found: C, 41.2; H, 6.00; F,

#### The reaction of Hexafluoropropene Oxide and Excess Methyllithium

Hexafluoropropene oxide (16.6 g., 0.10 mole) was condensed into a steel autoclave containing methyllithium (120 ml., 1.6M solution in ether, 0.20 mole). The autoclave was rocked whilst it attained room temperature (1 1/2 hours) and then for a further 24 hours. Absolute ethanol (20 ml.) was added and the autoclave was again rocked (1 1/2 hours). The reaction mixture was then poured onto ice-water/conc. HCl and the organic layer separated, washed with water (3 x 100 ml.) then dried (MgSO<sub>4</sub>). The ether was removed by rapid distillation. Fractionation of the remaining material using a spinning band column afforded a first fraction b.p. (74 mm.) 54-56° (15.0 g) which became solid when stored at 3-5°, and a second fraction b.p. (46 mm) 72-73° (12.0 g.) which showed a strong ir absorption at 5.70 μ. The lower boiling product

was identified as the carbinol  $\text{CF}_3\text{CF}(\text{CH}_3)\text{C}(\text{CH}_3)_2\text{OH}$  (15.0 g., 0.086 mole, 43%) by comparison with a known pure sample. The higher boiling material was identified as  $\text{CF}_3\text{CF}(\text{OCH}_2\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_3$  (12.0 g., 0.55 mole, 28%).

Reaction of Ethyllithium and HFPO (24.9 g., 0.15 mole) was condensed into an autoclave containing ethyllithium (455 ml 1.1 M solution in benzene  $\approx$  0.5 mole) (ex Alfa Inorganics). The autoclave was rocked whilst attaining room temperature (2 hr.) and then for a further 24 hrs at 50-55°. The autoclave was cooled and methanol (30 ml.) was added to the contents with stirring, the contents of the autoclave were then poured onto ice/water/conc HCl, the organic material was separated and dried ( $\text{CaSO}_4$ ). After removal of solvents, spinning band distillation of the remaining material yielded the carbinol  $\text{CF}_3\text{CFEtCEt}_2\text{OH}$  (16.8 g., 0.078 mole, 52%) b.p. 92-95° at 48 min. Hg.

Anal. Calcd for  $\text{C}_9\text{H}_{16}\text{F}_4\text{O}$ : C, 50.0; H, 7.41; F, 35.2.

Found: C, 50.3; H, 7.8; F,

$^1\text{H}$  nmr showed absorption assigned to two equivalent ethyl groups, one ethyl group in a different environment, and OH (6.92 $\tau$ ).  $^{19}\text{F}$  nmr (TFA ref.) showed absorption at -6.1 ppm (doublet,  $\text{CF}_3$ ,  $J=6.0$  Hz) and +100.0 ppm (complex, CF). The infrared and mass spectra were consistent with the proposed structure.

The reaction of n-propyllithium and hexafluoropropene oxide.

n-propyllithium was prepared by the addition of n-propyl chloride (39.0 g, 0.50 mole) to lithium sand (7.0 g., 1.0 g. atom) in sodium dried hexane, the rate of addition was adjusted to keep



a constant reflux. The solution of n-propyllithium was filtered and placed in a 1.21 autoclave under dry nitrogen. The autoclave was cooled to  $-196^{\circ}$  and evacuated, hexafluoropropene oxide (25.0 g., 0.15 mole) was condensed in and the autoclave was rocked at  $60^{\circ}$  (8 hr) then cooled and opened. The contents were poured into ice water/conc HCl, the hexane layer was separated, washed with water, and dried ( $\text{CaSO}_4$ ). Hexane was removed by distillation. The remaining material was fractionated under vacuum to yield  $\text{CF}_3\text{CF}(\text{n-Pr})\text{C}(\text{n-Pr})\text{OH}$  bp  $83-86^{\circ}$  (5 mm Hg) (17.8 g., 0.68 mole, 45%).

Anal. calcd for  $\text{C}_{12}\text{H}_{22}\text{F}_4\text{O}$ : C, 55.8; H, 8.53; F, 2945.

Found: C, 55.8; H, 8.56; F,

The  $^1\text{H}$  nmr spectrum was consistent with the proposed structure.  $^{19}\text{F}$  nmr spectroscopy showed absorption at  $-6.0$  ppm ( $\text{CF}_3$ , doublet,  $J=6.5$  Hz) and  $+99.0$  ppm (CF, complex). Infrared and mass spectrometry confirmed the proposed structure.

#### The reaction of n-butyllithium and HFPO

HFPO (33.2 g., 0.20 mole) was condensed into a steel autoclave containing n-butyllithium (384 ml 1.6 M solution  $\approx$  0.60 mole) (ex Foote Mineral Co.). The autoclave was rocked whilst attaining room temperature, then at  $50-55^{\circ}$  (24 hr). The autoclave was opened and the contents poured into ice-water/conc HCl. The organic layer was separated and dried, solvents removed by distillation. Fractional distillation of the remaining material yielded  $\text{C}_4\text{H}_9\text{CF}_2\text{C}(\text{OH})(\text{C}_4\text{H}_9)\text{CF}_3$  ( g., mole, %) bp  $39-40^{\circ}$  (0.8 mm Hg).

Anal. calcd for  $\text{C}_{11}\text{H}_{19}\text{F}_5\text{O}$ : C, 50.37; H, 7.26.

Found: C, 51.23; H, 7.23.

$^1\text{H}$  nmr showed complex absorption between 8.0 and 9.6 $\tau$ , and absorption due to OH.  $^{19}\text{F}$  nmr showed absorption at  $+1.1$  ppm ( $\text{CF}_3$ , singlet) and

+43.2 ppm ( $\text{CF}_2$ , triplet). Infrared and mass spectrometry were consistent with the assigned structure.

Preparation of *n*-pentyllithium and reaction with hexafluoropropene oxide

*n*-Pentyllithium was prepared from lithium sand (7.0 g., 1.0 g. atom) and 1-chloropentane (53.0 g., 0.50 mole) in hexane (sodium dried - 400 ml). This mixture was refluxed whist addition of 1-chloropentane was carried out, then refluxed for a further two hours, then filtered. The *n*-pentyllithium obtained was placed in a 1.2 liter autoclave which was sealed, cooled to  $-196^\circ$  and evacuated. Hexafluoropropene oxide (24.9 g., 0.15 mole) was condensed into the autoclave, which was rocked at room temperature 3 hours, then at  $60^\circ$  (8 hrs). Upon opening the contents were poured into ice-water/conc. HCl, the organic layer was separated, dried ( $\text{CaSO}_4$ ) then hexane was removed by distillation. Distillation of the remaining material yielded  $\text{CF}_3\text{CF}(\underline{n}\text{-Pt})\text{C}(\underline{n}\text{-Pt})_2\text{OH}$  (22.6 g, 0.066 mole, 44%) purified by preparative scale glc and characterized by nmr spectroscopy.

Reaction of Hexafluoropropene Oxide and Pentafluorophenyllithium.

Pentafluorophenyllithium was prepared by the addition of *n*-butyllithium (126.0 ml. 1.6 M solution; 0.20 mole) at  $-78^\circ$  to pentafluorobenzene (33.6 g., 0.20 mole) in ether (50 ml.) at  $-78^\circ$  with rapid stirring. The reaction mixtrue was maintained at  $-78^\circ$  (2 hr.) then hexafluoropropene oxide (33.2 g., 0.20 mole) was added via a dry ice/acetone condenser (0.5 hr.).  $-78^\circ$  was maintained for a further 4 hr. then the reaction mixture was warmed slowly to room temperature (5 hr.) and poured into ice-water/conc. HCl.

The organic layer was separated, washed with water (3 x 100 ml) then dried ( $\text{MgSO}_4$ ). After removal of ether and hexanes, a semi-solid material remained which is at present under investigation. Unreacted hexafluoropropene oxide (ca. 15 g.) and butane were collected in an external trap cooled to  $-78^\circ$  during the reaction.

#### Attempted Reaction of Hexafluoropropene Oxide and Trifluorovinyl lithium

Trifluorovinyl lithium was prepared by condensation of trifluoroethylene (16.4 g., 0.20 mole) into *n*-butyllithium (126 ml., 1.6M solution in hexanes, 0.20 mole) in dry ether (130 ml.) at  $-78^\circ$ .

Hexafluoropropene oxide (33.2 g., 0.20 mole) was condensed into the trifluorovinyl lithium solution at  $-78^\circ$  via a dry-ice/acetone condenser. The reaction mixture was maintained at  $-78^\circ$  (3 hr.), then warmed very slowly, at ca.  $-55^\circ$  the reaction mixture began to blacken rapidly. Unreacted hexafluoropropene oxide (ca. 15 g.) and butane were collected in an external trap cooled to  $-78^\circ$ . Methanol (20 ml.) was added to the reaction mixture which was then poured onto ice-water/conc. HCl, the organic layer was separated, washed with water (3 x 100 ml) then dried ( $\text{MgSO}_4$ ). After removal of ether and hexanes, a viscous tar remained which was not investigated further.

#### Preparation of $\text{CF}_3\text{C}\equiv\text{CH}$

Zinc dust (162.5 g., 2.5 g. atoms), zinc chloride (17.0 g., 0.125 mole) and freshly distilled N,N-dimethyl formamide (500 ml) were placed in a flask fitted with a mechanical stirrer, addition funnel, thermometer, and reflux condenser leading to a dry-ice

cooled trap. The flask was heated to  $100^{\circ}$  and addition of  $\text{CF}_3\text{CCl}=\text{CCl}_2$  (250 g., 1.25 moles) was commenced, the heat was removed and the rate of addition of olefin adjusted to maintain a temperature of  $95-105^{\circ}$  (2 hr. addition time). The reaction mixture was cooled to  $50-60^{\circ}$  and the slow addition of water (500 ml) was commenced, a vigorous gas evolution ensued and the gas was collected in the  $-78^{\circ}$  cold trap. I.r. spectroscopy indicated that the product which condensed at  $-78^{\circ}$  was 1,1,1-trifluoropropyne,  $\text{CF}_3\text{C}\equiv\text{CH}$  (85.5 g., 0.91 mole, 73%).

Attempted reaction of HFPO and 3,3,3-trifluoropropynyllithium

A flask was fitted with magnetic stirrer, addition funnel, dry ice condenser and nitrogen inlet tube. Dried ether (500 ml) was placed in the flask and cooled to  $-78^{\circ}$ . 3,3,3-trifluoropropyne,  $\text{CF}_3\text{C}\equiv\text{CH}$  (18.8 g., 0.20 mole) was condensed into the flask. n-Butyllithium (120 ml, 1.6 M solution in hexanes  $\approx$  0.20 mole) was added over 1 hour at  $-78^{\circ}$ . The solution was stirred at  $-60^{\circ}$  (2 hr) then HFPO (11.60 g., 0.07 mole) was condensed into the flask vis the dry ice acetone condenser. The mixture was stirred at  $-78^{\circ}$  (3 hr) then allowed to attain ambient temperature (8 hr). A large amount of black solid material became apparent in the flask. The mixture was poured onto ice-water/conc. HCl and the organic material extracted with ether, the ether extract was dried ( $\text{CaSO}_4$ ), and the solvents removed to yield a black viscous material which was not investigated further.

Preparation of  $\alpha$ -Bromotetrafluoropropionyl Fluoride.- Diglyme (40 ml., distilled from  $\text{LiAlH}_4$  and stored over 4A molecular sieve) and vacuum dried lithium bromide were placed in a Fisher-Porter tube which was evacuated and cooled to  $-196^{\circ}$ . HFPO (16.6g., 0.10 mole)

was condensed into the tube. The tube was sealed and shaken at room temperature (ca. 28°, 8 hr.). The tube was then opened in vacuo and  $\alpha$ -bromo tetrafluoropropionyl fluoride,  $\text{CF}_3\text{CBrF.COF}$  (21.0 g., 0.092 mole, 92%) was collected in a trap cooled to -78°.

#### Reaction of $\text{CF}_2=\text{CFCOF}$ and trifluorovinyl lithium

Trifluorovinyl lithium was prepared by reaction of n-butyllithium (256 ml, 1.6 M solution in hexanes) and  $\text{Et}_2\text{O}$  (120 ml) with trifluoroethylene (33.0 g., 0.40 mole) at -78°. Trifluoroethylene was added via a dry-ice/acetone condenser, the solution was stirred at -78° (2 hr.) before addition of  $\text{CF}_2=\text{CFCOF}$ . A solution of  $\text{CF}_2=\text{CFCOF}$  (10.0 g., 0.085 mole) in  $\text{Et}_2\text{O}$  (20 ml) at -78° was added slowly (1 1/2 hr) to the solution of trifluorovinyl lithium. A vigorous reaction occurred and solid material became apparent in the reaction flask. After addition the mixture was warmed to room temperature (4 hrs.) during which time rapid blackening of the mixture occurred. The mixture was poured into ice water/conc HCl, the ether layer was separated, washed with water and dried. After removal of ether and hexanes, only tarry material remained-no products were isolated from this tar.

#### The reaction of $\text{CF}_3\text{CBrFCO}_2\text{Me}$ and Butyllithium

$\text{CF}_3\text{CBrFCO}_2\text{Me}$  (23.9 g., 0.10 mole) in dry ether (50 ml.) was added to a stirred solution of n-butyllithium (187.0 ml., 1.6M solution in hexanes, 0.30 mole) in dry ether (100 ml.) in an

atmosphere of nitrogen at  $-78^{\circ}$ . The reaction mixture was maintained at  $-78^{\circ}$  (3 hr.) and then warmed to room temperature (4 hr.) during which it darkened rapidly. Methanol (20 ml.) was added and the reaction mixture was poured onto ice-water/conc. HCl. The organic layer was separated, washed with water (2 x 100 ml.) and dried ( $\text{MgSO}_4$ ). After removal of ether and hexanes by fractional distillation, vpc of the remaining material indicated the presence of ca. 9 components. The mixture was not separated.

#### The Reaction of $\text{CF}_3\text{CBrFCOF}$ and Butyllithium

$\text{CF}_3\text{CBrFCOF}$  (28.0 g., 0.123 mole) in dry ether (50 ml.) was added to n-butyllithium (232 ml., 1.6M solution in hexanes, 0.37 mole) in dry ether (100 ml.) at  $-78^{\circ}$  (3 hr.) then warmed to room temperature (3 hr.) and stirred for a further 6 hours. Methanol (20 ml.) was added and the reaction mixture was poured onto ice-water/conc. HCl. The organic layer was separated, washed with water (3 x 100 ml.) then dried ( $\text{MgSO}_4$ ). Ether and hexanes were removed by fractional distillation. Vpc of the remaining material indicated the presence of two components in the approx. ratio 6:1. A spinning band distillation of this mixture is in progress and an nmr investigation of the products will be carried out.

#### Attempted Reaction of Methyl- $\alpha$ -bromotetrafluoropropionate and

Zinc.- Zinc dust (2.3 g., 0.035 g. atom), benzaldehyde (3.6 g.) and benzene (30 ml.) were placed in a flask fitted with reflux condenser, magnetic stirrer and dropping funnel. Methyl- $\alpha$ -bromotetrafluoropropionate (8.0 g., 0.032 mole) was added and the reaction mixture refluxed (48 hours) then cooled and filtered. V.p.c. indicated the presence only of uncharged reactants.

Attempted Addition of Dibromodifluoromethane to 1,2-dichloro-1,2-difluoroethylene.- Dibromodifluoromethane (840.0 g., 4.0 moles), 1,2-dichloro-1,2-difluoroethylene (133.0 g., 1.0 mole) and benzoyl peroxide (5.0 g.) were sealed into a 1.3 l. steel autoclave and heated at 100-105° (5 hr.). Fractional distillation of the contents after reaction yielded unchanged dibromodifluoromethane and a mixture (30 g.) which was shown by v.p.c. to consist of four major components.

Addition of  $\text{CBrF}_2\text{CBrClF}$  to Ethylene.

$\text{CBrF}_2\text{CBrClF}$  (553.0 g., 2.0 moles) was placed in a 100° ml flask fixed with a reflux condenser, magnetic stirrer and gas inlet tube. Benzoyl peroxide (10.0 g.) was added and the contents of the flask heated to reflux temperature. Ethylene was bubbled into the solution (12 hr.). Fractional distillation of the reaction products yielded unreacted  $\text{CBrF}_2\text{CBrClF}$  (150.0 g., 0.54 mole, 27%), the required adduct  $\text{CBrF}_2\text{CClFCH}_2\text{CH}_2\text{Br}$  (402 g., 1.32 mole, 66%) and viscous telomeric material ca. 35 g.

Dehydrohalogenation of  $\text{CBrF}_2\text{CClFCH}_2\text{CH}_2\text{Br}$

Potassium hydroxide (250 g.) and water (550 ml.) were placed in a flask which was fitted with a mechanical stirrer, dropping funnel and reflux condenser. The solution was heated to reflux temperature and  $\text{CBrF}_2\text{CClFCH}_2\text{CH}_2\text{Br}$  (158.0 g., 0.52 mole) was added (2 hr.). The reaction mixture was stirred at reflux temperature (6 hr.) and then the organic products were steam distilled from the reaction mixture. After separation from water and drying ( $\text{MgSO}_4$ ), fractional distillation yielded  $\text{CBrF}_2\text{CClFCH}=\text{CH}_2$  (85.0 g., 0.38 mole, 73%) b.p. 98-100° and unreacted  $\text{CBrF}_2\text{CClFCH}_2\text{CH}_2\text{Br}$  (24.0g., 0.08 mole, 15%).

### Oxidation of $\text{CBrF}_2\text{CClFCH=CH}_2$

Potassium permanganate (336.0 g., 2.1 moles) and water (2000 ml.) were placed in a flask fitted with a reflux condenser, stirrer and an addition funnel. The mixture was stirred at  $60^\circ$  and  $\text{CBrF}_2\text{CClFCH=CH}_2$  (151.0 g., 0.68 mole) was added (2 hr.). The reaction mixture was stirred at  $60^\circ$  (6 hr.), cooled to  $0^\circ$  and acidified with dilute sulphuric acid, then treated with sodium bisulphite solution (10%) and extracted with ether (3 x 200 ml). The ether extract was dried ( $\text{MgSO}_4$ ) and the ether was removed by rapid distillation. Fractional distillation of the remaining material yielded  $\text{CBrF}_2\text{CClFCO}_2\text{H}$  (80.5 g., 0.33 moles, 49%) b.p.  $78-81^\circ$  (5.0 mm.).

### Attempted reaction of $\text{CBrF}_2\text{CClFCO}_2\text{H}$ and KF/benzoyl Chloride.

Benzoyl chloride (100 ml.) and dried potassium fluoride (11.60 g., 0.20 mole) were placed in a flask which was fitted with a magnetic stirrer, addition funnel and a reflux condenser connected to an external trap cooled to  $-78^\circ$ . The mixture was heated to ca.  $80^\circ$  and  $\text{CBrF}_2\text{CClFCO}_2\text{H}$  was added slowly (24.1 g., 0.10 mole). On heating the mixture to reflux temperature, ca. 1.0 g. of the acid fluoride  $\text{CBrF}_2\text{CFCOCl}$  condensed in the external trap.

### Reaction of $\text{CBrF}_2\text{CClFCO}_2\text{H}$ and Phosphorous Pentachloride

$\text{CBrF}_2\text{CClFCO}_2\text{H}$  (24.1 g., 0.10 mole) was dropped onto phosphorous pentachloride under anhydrous conditions. The reaction flask was heated to allow the acid chloride formed to distill out.  $\text{CBrF}_2\text{CClFCOCl}$  (18.5 (18.5 g., 0.07 mole, 70%) b.p.  $88-89^\circ$  was obtained together with a small amount of phosphorous oxychloride,  $\text{POCl}_3$ , which was separated by freezing out.



Preparation of  $\text{CBrF}_2\text{CClFCO}_2\text{Me}$ .

$\text{CBrF}_2\text{CClFCOCl}$  (18.5 g., 0.07 mole) was dropped slowly into methanol (ca. 50 ml) which was cooled to  $5^\circ$ . After addition the reaction mixture was stirred for 3 hr. at  $30^\circ$  and then poured into water. The ester layer was separated and washed with water (3 x 50 ml.) then dried ( $\text{CaSO}_4$ ). The ester  $\text{CBrF}_2\text{CClFCO}_2\text{Me}$  (15.2 g., 0.06 mole, 85%) was identified by i.r. spectroscopy.

The Formation of  $\text{CF}_2\text{BrCFC1CO}_2\text{Me}$

$\text{CF}_2\text{BrCFC1CO}_2\text{H}$  (70.0 g., 0.29 mole) was placed in a flask fitted with a reflux condenser, addition funnel and magnetic stirrer.  $\text{SOCl}_2$  (35.7 g., 0.30 mole) and pyridene (3 drops) were added and the contents of the flask refluxed (20 hr). After evolution of  $\text{HCl}$  and  $\text{SO}_2$  ceased, methanol (ca. 25 ml) was added dropwise to the reaction products which were cooled in ice/water. The reaction mixture was stirred for 16 hours with excess methanol then poured into water. The organic material was separated, washed with water, then dried ( $\text{CaSO}_4$ ). Fractional distillation of the organic material yielded  $\text{CF}_2\text{BrCFC1CO}_2\text{Me}$  (46.0 g., 0.18 mole, 62%), bp  $70-73^\circ$  (57 mm). The purity of this material was confirmed by glc analysis.

Attempted dehalogenation of  $\text{CF}_2\text{BrCFC1CO}_2\text{Me}$

$\text{CF}_2\text{BrCFC1CO}_2\text{Me}$  (40.0 g., 0.16 mole) was added with rapid stirring to zinc dust (32.5 g., 0.50 g. atom) in methanol (250 ml). (Zinc dust was previously activated by washing with 5%  $\text{HCl}$ , 3x water, and 6x methanol). Reaction was started with difficulty, then appeared to continue smoothly. After completion of addition of  $\text{CF}_2\text{BrCFC1CO}_2\text{Me}$ , reaction mixture was left to reflux (8 hr.), however, during this time an explosion occurred and all material was lost.

### Formation of $\text{CF}_2=\text{CFCO}_2\text{Li}$

n-BuLi (320 ml in hexanes, 1.6M solution=0.50 mole) and ether (300 ml) were placed in a flask fitted with dry-ice condenser, magnetic stirrer and a nitrogen sweep. The mixture was cooled to  $-78^\circ$  and  $\text{CHF}=\text{CF}_2$  (41.0 g., 0.50 mole) was condensed with the flask via the dry-ice condenser. The solution was stirred at  $-78^\circ$  for 1 hour to allow the exchange to take place. Carbon dioxide, previously dried by passage through a tower of anhydrous  $\text{CaSO}_4$ , was bubbled into the solution of  $\text{CF}_2=\text{CFLi}$  (1 hr.). The reaction mixture was then allowed to attain ambient temperature (6 hr.). The solvents were removed in vacuo to yield a yellowish powder,  $\text{CF}_2=\text{CFCO}_2\text{Li}$  (56.0 g., p.43 mole, 86%) which was dried over phosphorous pentoxide in vacuo.

### Attempted formation of $\text{CF}_2=\text{CFCOCl}$ .

$\text{CF}_2=\text{CFCO}_2\text{Li}$  (10.0 g., 0.08 mole) was placed in a flask containing phosphorous pentachloride (ca. 15 g) in carbon tetrachloride. The contents were heated with stirring to  $70^\circ$  during which the contents of the flask darkened rapidly. No material was collected in an external trap cooled to  $-78^\circ$ .

### Preparation of $\text{CF}_2=\text{CFCO}_2\text{H}$

$\text{CF}_2=\text{CFCO}_2\text{Li}$  was prepared by the procedure described above using 0.5 mole quantities of reactants. Hydrolysis of this salt was carried out using 50% conc. HCl/water. A visious liquid was obtained which was dried in vacuo, this material was shown by ir spectroscopy to be crude  $\text{CF}_2=\text{CFCO}_2\text{H}$  (41.5 g., 0.33 mole, 65%).

Attempted direct esterification of  $\text{CF}_2=\text{CFCO}_2\text{Li}^5$ .

$\text{CF}_2=\text{CFCO}_2\text{Li}$  (20.0 g., 0.15 mole) was placed in a flask fitted with a reflux condenser, addition funnel and a magnetic stirrer. A mixture of conc.  $\text{H}_2\text{SO}_4$  (5 ml.) and methanol (20 ml.) was added slowly and the reaction mixture was stirred at  $30^\circ$  (5 hr). The reaction mixture was then poured into ice-water and the organic material extracted with ether. The ether extract was washed with 5%  $\text{Na}_2\text{CO}_3$  solution to remove free acid, then dried ( $\text{CaSO}_4$ ). The ether was removed by distillation. On fractional distillation of the remaining material decomposition occurred and a black residue remained. No  $\text{CF}_2=\text{CFCO}_2\text{Me}$  was obtained.

Attempted formation of  $\text{CF}_2=\text{CFCOCl}$  and reaction with methanol.

Crude  $\text{CF}_2=\text{CFCO}_2\text{H}$  (32.0g., 0.25 mole) was dropped slowly onto phosphorous pentachloride (104.0 g., 0.50 mole). Gases evolved were taken into ice cooled methanol via an ice-water condenser. The reaction flask was heated to ca.  $60^\circ$ . After evolution of gas had ceased, the methanol was poured into water and no organic material remained.

Preparation of  $\text{CF}_2=\text{CFCO}_2\text{Ag}$

A solution of silver nitrate (85.0 g., 0.50 mole) in water (300 ml) was added slowly to a stirred suspension of  $\text{CF}_2=\text{CFCO}_2\text{Li}$  (65.0 g., 0.49 mole) in water (200 ml). A white solid precipitate was formed, the reaction mixture was stirred at  $30^\circ$  (16 hr). The solid was filtered, washed with water, then dried over phosphorous pentoxide in vacuo.

Reaction of  $\text{CF}_2=\text{CFCO}_2\text{Ag}$  and Methyl iodide

Dry  $\text{CF}_2=\text{CFCO}_2\text{Ag}$  (117.0 g., 0.50 mole), methyl iodide (75.0 g., 0.53 mole) and Freon 113 (170 ml) were placed in a flask fitted with a magnetic stirrer and reflux condenser. The mixture was stirred at room temperature (10 hr.) during which time a fine pale yellow precipitate of silver iodide became apparent.

The reaction mixture was then filtered through celite the Freon 113 was removed by distillation. Fractional distillation of the remaining material yielded a fractional, bp  $85-86^\circ$  (6.0 g., 0.043 mole, 9%) which was shown by ir spectroscopy and glc analysis to be  $\text{CF}_2=\text{CFCO}_2\text{Me}$ . Higher boiling materials which were not investigated were also obtained.

Attempted reaction of trifluoromagnesium bromide and diethyl carbonate

Magnesium turnings (12.0 g., 0.50 atom) and THF (200 ml.) which had been freshly distilled from sodium metal were placed in a flask fitted with a magnetic stirrer, cooled addition funnel and a dry-ice condenser. Trifluorovinylmagnesium bromide was prepared by the addition of  $\text{CF}_2=\text{CFBr}$  (80.5 g., 0.50 mole) in THF to the magnesium metal at ca.  $-20^\circ \rightarrow 10^\circ$ .

Diethyl carbonate (59.0 g., 0.50 mole) was then added to the THF solution of Grignard reagent at  $-20^\circ$  (1 hr.). The mixture was allowed to attain room temperature overnight and was then poured into water. The organic material was extracted with ether, the ether extract was dried ( $\text{CaSO}_4$ ). Distillation of this material yielded, in addition to ether and THF, only unreacted diethyl carboante and a tarry material. No  $\text{CF}_2=\text{CFCO}_2\text{Et}$  was obtained.

Attempted reaction of trifluorovinyl lithium and ethyl chloroformate.

$\text{CF}_2=\text{CFLi}$  was prepared as described previously by the addition of  $\text{CHF}=\text{CF}_2$  (41.0 g., 0.50 mole) to  $n\text{-BuLi}$  in ether. The mixture was stirred for 2 hr at  $-78^\circ$  to allow exchange to take place, then it was cooled to  $-120^\circ$  (ether/liquid nitrogen slush). Ethyl chloroformate (64.2g., 0.50 mole) in ether (100 ml), precooled to  $-78^\circ$  was added slowly (1 hr.). The mixture was then allowed to obtain room temperature (6 hr). The mixture was filtered and the ether and hexanes were removed by distillation. Distillation of the remaining material using a spinning band column afforded diethylcarbonate bp  $125^\circ$  (14.0 g., 0.12 mole, 24%) and a visious residue which was not investigated further. Diethylcarbonate obtained was identified by an ir and glc comparison with an authentic sample.

Preparation of Trifluoroacetyl Chloride

Phosphorous pentachloride (120 g) was placed in a flask fitted with an addition funnel and reflux condenser. Trifluoroacetic acid (50.0 g., 0.51 mole) was dropped onto the phosphorous pentachloride (2 hours), and the gas evolved was taken via the reflux condenser into an external trap cooled to  $-78^\circ$ . Trifluoroacetyl chloride (54.0 g., 0.41 mole, 80%) was identified by i.r. spectroscopy.

Attempted Reaction of  $\text{CF}_3\text{COCl}$  and Trifluoroethylene.

A 120 ml capacity steel autoclave was loaded with anhydrous aluminium chloride (13.3 g., 0.10 mole) and carbon tetrachloride (30 ml). The autoclave was sealed, cooled to  $-196^\circ$  and evacuated.  $\text{CF}_3\text{COCl}$  (40.0 g., 0.30 mole) and  $\text{CHF}=\text{CF}_2$  (12.3 g., 0.15 mole) were condensed in. After attaining room temperature, the autoclave

was heated at  $60^{\circ}$  ( $\pm 5^{\circ}$ ) (6 hr.). The bomb was then cooled in ice/water and the volatile contents vented into an external trap at  $-78^{\circ}$ . The remaining contents of the bomb were poured into ice/conc HCl and the  $\text{CCl}_4$  layer was separated, washed with water, then dried ( $\text{CaSO}_4$ ). G.l.c. did not indicate the presence of any adducts.

The Attempted Reaction of  $\text{CF}_2=\text{CFCO}_2\text{Li}$  and Iodoethane.

The lithium salt of perfluoroacrylic acid was prepared by the method described in previous reports. The salt was dried over phosphorous pentoxide in vacuo (4 days).

$\text{CF}_2=\text{CFCO}_2\text{Li}$  (20.0 g., 0.15 mole) and iodoethane (50.0 g., 0.51 mole) were placed in a flask fitted with a reflux condenser and magnetic stirrer, and refluxed (6 hr.). ca. 0.1 g. hydroquinone was added to inhibit polymerization. No  $\text{CF}_2=\text{CFCO}_2\text{Et}$  was obtained.

Attempted bromination of perfluoroacrylic acid.

Perfluoroacrylic acid (100.0 g., 0.80 mole) in  $\text{CCl}_4$  (300 ml) was placed in a flask fitted with a magnetic stirrer, addition funnel and reflux condenser. Bromine (128.0 g., 0.80 g. atom) was added slowly to the reaction mixture which was refluxed and irradiated with a u.v. lamp. The bromine color was not discharged at all.

Preparation of  $\text{CFCl}=\text{CFCl}$

Freon 112 ( $\text{CFCl}_2\text{CFCl}_2$ ) (2700 g., 13.0 moles) and isopropanol (2000 g., 31.0 g. atoms) in iso-propanol (2.5 l) to which zinc chloride (50 g) had been added. The gas evolved was collected in traps cooled to  $-78^{\circ}$ , and was shown by i.r. spectroscopy to be  $\text{CFCl}=\text{CFCl}$  (1520 g., 11.4 moles, 83 %).

Reaction of  $\text{CFCl}_3$  and  $\text{CFCl}=\text{CFCl}$

Freon 11 ( $\text{CFCl}_3$ ) (1490 g., 11.80 moles) and aluminium chloride (70.0 g., 0.50 moles) were placed in a flask fitted with a dry ice condenser and stirrer. The temperature was maintained at  $18-20^\circ$  and  $\text{CFCl}=\text{CFCl}$  was distilled from phosphorous pentoxide into the flask. The reaction mixture blackened and was stirred at  $18-20^\circ$  (10 hr) then refluxed (3 hr.). 50% HCl (400 ml) was added to the flask and the organic material was separated. Distillation of this material yielded the required adducts, b.p.  $150-153^\circ$  (1340 g.).

Dehalogenation of  $\text{C}_3\text{Cl}_5\text{F}_3$  fraction from  $\text{CFCl}_3 + \text{CFCl}=\text{CFCl}$

A 5-liter flask was fitted with a mechanical stirrer, a Dean-Stork head summounted by a reflux condenser, and an addition funnel. Ethanol (3l.) zinc dust (1300 g, 20.0g. atoms) and zinc chloride (ca 10 g) were placed in the flask and heated to reflux temperature. The  $\text{C}_3\text{Cl}_5\text{F}_3$  fraction in ethanol (2670 g., 9.9 moles) was added dropwise and the ethanol/product mixture distilled out continuously during the reaction. After washing with water, the product was dried ( $\text{MgSO}_4$ ) and rectified to yield  $\text{C}_3\text{F}_3\text{Cl}_3$  b.p. (710.0g., 3.56 moles 36%) which was characterized by ir spectroscopy.

Bromination of  $\text{CF}_2\text{ClCF}=\text{CCl}_2$

$\text{CF}_2\text{ClCF}=\text{CCl}_2$  (273.0 g., 1.37 moles) was placed in a vycor flask which was fitted with a reflux condenser, magnetic stirrer and addition funnel. Bromine (220.0 g., 1.38 g. atoms) was added whilst the contents of the flask were maintained at ca.  $60^\circ$ , and irradiated with a sun-lamp (4 hr.). The crude product was taken

into Freon 113 and washed with 10% aqueous sodium bisulphite solution, then washed with water and dried ( $\text{CaCl}_2$ ). Freon 113 was removed by distillation. Fractional distillation of the remaining material yielded  $\text{CF}_2\text{ClCFBrCCl}_2\text{Br}$  (353 g., 1.03 moles, 75%) bp  $81-82^\circ$ , 17 mm. Hg.

#### Hydrolysis of $\text{CF}_2\text{ClCFBrCCl}_2\text{Br}$

Fuming sulphuric acid (86 ml. 45%  $\text{SO}_3$ ) was placed in a flask which was fitted with a magnetic stirrer, reflux condenser connected to a sulphuric acid bubbler and an addition funnel.  $\text{CF}_2\text{ClCFBrCCl}_2\text{Br}$  (353 g., 1.03 moles) and ca. 1.0 g mercuric oxide catalyst were added to the flask. The reaction mixture was stirred at ambient temperature (16 hr), then at  $80^\circ$  (16 hr) and finally at  $100^\circ$  (16 hr). The reaction flask was fitted with distillation apparatus and crude acid chloride was distilled out at  $100-108^\circ$ . fractional distillation of the crude product afforded  $\text{CF}_2\text{ClCFBrCOCl}$  (205 g., 0.79 mole, 77%) which was characterized by i.r. spectroscopy.

#### Preparation of $\text{CF}_2\text{ClCFBrCOF}$

$\text{CF}_2\text{ClCFBrCOCl}$  (90 g., 0.35 mole) and an equimolar mixture of antimony pentachloride and antimony trifluoride (186.0 g) were placed in a flask fitted with fractionating column and partial take-off head. The flask was heated on an oil bath to  $104^\circ$ , and maintained at this temperature (2hr.), during which time a liquid b.p.  $64-66^\circ$  distilled off. The flask was heated to  $130^\circ$  and more liquid b.p.  $64-66^\circ$  distilled off. Fractional distillation of this liquid yielded  $\text{CF}_2\text{ClCFBrCOF}$  (70.5 g., 0.29 mole, 83%) b.p.  $65-66^\circ$ , which was identified by i.r. spectroscopy.

#### Dehalogenation of $\text{CF}_2\text{ClCFBrCOF}$

$\text{CF}_2\text{ClCFBrCOF}$  (45.0 g., 0.18 mole) in anhydrous dioxane (40 ml.) was added over 4 hr. to zinc dust (20.0 g., 0.32 g. atom) in dioxane (100 ml.) at  $100^\circ$  with rapid



stirring. The gas evolved was taken via a reflux condenser and condensed in a trap cooled to  $-78^{\circ}$ . The mixture was refluxed for 5 hrs. The condensed material was fractionally distilled to yield  $\text{CF}_2=\text{CFCOF}$  (17.0 g., 0.13 mole, 74%) b.p.  $23-28^{\circ}$ , which was identified by i.r. and n.m.r. spectrometry.

#### Preparation of $\text{CF}_2\text{ClCFBrCO}_2\text{Me}$

$\text{CF}_2\text{ClCFBrCOCl}$  (43.0 g., 0.165 mole) was added slowly (1 hr.) to ice-cold methanol (120 ml). The mixture was refluxed (2 hr.) then Freon 113 was added (150 ml) and the material washed with water (3 x 200 ml), then dried ( $\text{CaCl}_2$ ). After removal of Freon 113, fractional distillation yielded  $\text{CF}_2\text{ClCFBrCO}_2\text{Me}$  (39.0 g., 0.153 mole, 93%) which was identified by i.r. spectroscopy.

#### Preparation of $\text{CF}_2=\text{CFCO}_2\text{Me}$

Copper activated zinc dust (27.0 g., 0.41 g. atom) was placed in a flask together with anhydrous ether (120 ml.). The mixture was heated to reflux with rapid stirring and  $\text{CF}_2\text{ClCFBrCO}_2\text{Me}$  (39.0 g., 0.153 mole) was added dropwise (1 hr.), and the mixture was stirred for a further 3 hrs. under reflux. The mixture was then filtered and the ether was removed by distillation. The remaining material was taken into another flask in vacuo, fractional distillation of this material yielded  $\text{CF}_2=\text{CFCO}_2\text{Me}$  (12.0 g., 0.086 mole, 57%) b.p.  $85-87^{\circ}$ , which was characterized by i.r. and n.m.r. spectroscopy.

#### Investigation of the reaction of ammonia and hexafluoropropene.

Ammonia and hexafluoropropene (approx. 2:1 ratio by volume) were passed through a glass tube (3 1/2 ft. x 1" i.d.). No reaction occurred even when the tube was heated.

Ammonia (2.7 g., 0.16 mole) and hexafluoropropene (15.0, 0.10 mole) were condensed into a monel autoclave (capacity 80 ml.). The autoclave was warmed to

room temperature then rocked at this temperature (3 days). Upon opening no volatile products were present. A brown solid material was present in the autoclave, this was washed with water and extracted with ether. After drying, the ether was removed to yield a viscous tar.

#### Preparation of 1,1-dichloro-2,2-difluoroethylene

Freon 112A,  $\text{CClF}_2\text{CCl}_3$  (1835 g., 9.0 moles) in n-propanol (800 ml.) was added to zinc dust (975 g., 15.0 g. atoms) in refluxing n-propanol (2000 ml.) with rapid stirring. Anhydrous zinc chloride (ca. 2.0 g.) was added to initiate the reaction. The rate of addition of Freon 112A in n-propanol was adjusted to maintain refluxing.  $\text{CF}_2=\text{CCl}_2$  (1040 g., 07.8 moles, 87%) was collected in an external trap cooled to  $-78^\circ$  in dry ice/acetone after passage through a drying tower packed with anhydrous  $\text{CaSO}_4$ .

#### Bromination of 1,1-dichloro-2,2-difluoroethylene

Bromine (400.0 g., 2.50 g. atoms) was placed in a flask and stirred rapidly whilst the olefin  $\text{CF}_2=\text{CCl}_2$  was bubbled through a sintered disc (332.5 g., 2.50 mole). Addition of olefin was discontinued when the bromine color began to fade, with further stirring the color of bromine was discharged completely to leave  $\text{CF}_2\text{BrCCl}_2\text{Br}$  (705.0 g., 2.40 moles, 96%) which was identified by ir spectroscopy.

#### Oxidation of $\text{CBrF}_2\text{CBrCl}_2$

$\text{CBrF}_2\text{CBrCl}_2$  (600 g., 2.05 moles) was placed in a flask fixed with an addition funnel, magnetic stirrer and reflux condenser. Fuming sulphuric acid (450 ml. 40%) was added slowly (1 hr.). The

reaction mixture was heated to ca.  $90^{\circ}$  (3 hr.) and maintained at this temperature (3 days), the gases evolved were bubbled into methanol.

The methanol was added to water (500 ml.) and the organic layer separated, washed with water (3 x 300 ml.) then dried ( $\text{MgSO}_4$ ). Fractional distillation of this material afforded  $\text{CBrF}_2\text{CO}_2\text{Me}$  (230 g., 1.22 moles, 60%) b.p.  $94-98^{\circ}$ .

#### Preparation of $\text{CBrF}_2\text{CO}_2\text{Na}$ from $\text{CBrF}_2\text{CO}_2\text{Me}$

$\text{CBrF}_2\text{CO}_2\text{Me}$  (205 g., 1.08 mole) and ethanol (150 ml.) were placed in a flask which was fitted with a reflux condenser, magnetic stirrer and dropping funnel. A solution of potassium hydroxide (1.08 moles) in ethanol (100 ml.) was added to the contents of the flask (3 hrs). The reaction mixture was stirred (8 hrs) then cooled and ethanol was removed under vacuum. A white solid was obtained which will be reacted with conc. sulphuric acid to obtain the free acid,  $\text{CBrF}_2\text{CO}_2\text{H}$ .

#### Preparation of $\text{CF}_2\text{BrCO}_2\text{H}$

$\text{CF}_2\text{BrCO}_2\text{Na}$  (187.0 g., 0.95 mole) was placed in a 3 necked flask fitted with a magnetic stirrer addition funnel and distillation apparatus (air condenser). The receiver flask was cooled in dry ice/acetone and the apparatus was evacuated. Conc. sulphuric acid (98%) was slowly added to the contents of the flask, gentle heating was applied by means of an oil bath. A white solid condensed in the air condenser which, on warming, passed into the receiver flask. This white solid was identified as  $\text{CF}_2\text{BrCO}_2\text{H}$  by ir spectroscopy (1570 g., 0.90 moles, 95%).

### Preparation of $\text{CF}_2\text{BrCOCl}$

$\text{CF}_2\text{BrCO}_2\text{H}$  (148.0 g., 0.85 mole) and phosphorous pentachloride (208.5 g., 1.0 mole) were placed in a flask fitted with fractional distillation equipment and a magnetic stirrer. The flask was heated slowly in an oil-bath.  $\text{CF}_2\text{BrCOCl}$  (123.0 g., 0.64 mole) distilled (76%) from the flask (bp 30-35°) and was collected in a cooled receiver and identified by ir spectroscopy.

### Preparation of $\text{CF}_2\text{BrCOCl}$ directly from $\text{CF}_2\text{BrCCl}_2\text{Br}$ .

$\text{CF}_2\text{BrCCl}_2\text{Br}$  (300.0 g., 1.03 moles) was placed in a flask fitted with a reflux condenser, magnetic stirrer and addition funnel. Oleum (225 ml, 40%) was added slowly (1 hr.). The reaction mixture was heated to ca. 85° (3 hr.) and maintained at this temperature (3 days). The gases evolved were condensed in a cold trap cooled to -78° in dry ice/acetone. The contents of the cold trap were placed in a 3 necked flask, cooled to -78° and fitted with an addition funnel and distillation set-up. Anisole was dropped slowly into the flask which was allowed to warm to room temperature slowly. The bromine color was discharged and HBr was evolved, the required acid chloride  $\text{CF}_2\text{BrCOCl}$  was then distilled out at 30-35° (97.0 g., 0.51 mole, 49%) and was identified by ir spectroscopy.

### Preparation of $\text{CF}_2\text{BrCOF}$

$\text{CF}_2\text{BrCOCl}$  (85.0 g., 0.44 mole) was cooled to -78° and added slowly to  $\text{ZnF}_2$  (103.0 g., 1.0 mole) in diglyme (ca. 100 ml.) Volatile products were removed via an ice/water condenser and collected in a trap cooled to -78°. I.R. spectroscopy indicated the contents of the -78° trap to be  $\text{CF}_2\text{Br COF}$  (51.0 g., 0.33 mole, 76%).

### The Reaction of $\text{CF}_2\text{BrCOF}$ , $\text{F}^-$ and $\text{CF}_3\text{CF}(\text{O})\text{CF}_2$ .

A 120 ml autoclave was loaded with dry diglyme (30 ml) and dry CsF (8.0 g.). It was then sealed, cooled to  $-196^\circ$  and evacuated. The autoclave was maintained at  $-196^\circ$  while  $\text{CF}_2\text{BrCOF}$  (35.2 g., 0.20 mole) and  $\text{CF}_3\text{CF}(\text{O})\text{CF}_2$  (33.2 g., 0.20 mole) were condensed in. The autoclave was rocked at  $30^\circ$  (72 hrs), then cooled to  $-78^\circ$  and methanol (30 ml.) added. After attaining ambient temperature, the contents of the autoclave were poured into ice water and the organic layer was separated, washed with water (3 x 150 ml) then dried ( $\text{CaSO}_4$ ).

Distillation of this organic material using a spinning-band column afforded  $\text{CF}_3\text{CF}_2\text{CO}_2\text{Me}$  (23.5 g., 0.13 mole, 64%) bp  $59-61^\circ$ , and  $\text{CF}_2\text{BrCO}_2\text{Me}$  (24.0 g., 0.13 mole, 65%) bp  $95-96^\circ$ . Both products were characterized by ir and glc comparison with known pure samples.

### Reaction of hexafluoroacetone, iodide ion and hexafluoropropene oxide

Sodium iodide (15.0 g., 0.10 mole) which was previously vacuum dried and diglyme (ca. 40 ml) were placed in a Fisher-Porter tube which was then cooled to  $-196^\circ$  and evacuated. Hexafluoroacetone (16.6g, 0.10 mole) was condensed into the tube which was shaken at  $30^\circ$  for 48 hrs. The tube was again cooled to  $-196^\circ$  and hexafluoropropene oxide (16.6 g, 0.10 mole) was condensed into the tube which was again shaken at  $30^\circ$  (72 hrs). The tube was cooled in ice and methanol (ca. 15 ml) was taken into the tube which was shaken whilst attaining room temperature. The reaction mixture was poured into ice/water and the organic products were extracted with ether. The ether extract was dried ( $\text{CaCl}_2$ ) and the ether removed by distillation. Fractional distillation of the remaining material afforded  $\text{CF}_3\text{CHFCO}_2\text{Me}$  (3.0g) and  $(\text{CF}_3)_2\text{CF-O-CF}(\text{CF}_3)\text{CO}_2$

(19.5 g, 0.06 mole, 60%) b.p. 108-118°. The ir and nmr spectra of the major product were consistent with the proposed structure. A viscous residue remained which was not investigated further.

Attempted formation of  $\text{ICF}_2\text{O}^-$  and its reaction with hexafluoropropene Oxide

A 120 ml Monel autoclave was charged with dried sodium iodide (15.0 g., 0.10 mole) and dry diglyme (ca. 50 ml). The autoclave was cooled in liquid nitrogen and evacuated, carbonyl fluoride (8.5 g., 0.10 mole) was condensed into the vessel which was rocked at room temperature (72 hrs). The vessel was cooled to -78° and methanol (ca. 20 ml.) introduced. After warming to room temperature the contents were poured into water. The organic layer was extracted with ether, dried ( $\text{CaSO}_4$ ) and the ether removed by distillation. G.l.c. analysis of the remaining material (ca. 6 g) indicated a complex product mixture with no single component predominating, this was not investigated further.

Reaction of hexafluoroacetone, iodide ion and hexafluoropropene oxide

Sodium iodide (dried; 15.0 g, 0.10 mole) and diglyme (ca. 30 ml) were placed in a Fisher-Porter tube which was then cooled to -196° and evacuated. Hexafluoroacetone (16.6 g., 0.10 mole) was condensed into the tube which was then shaken at room temperature (ca. 30°) for 48 hrs. The tube was again cooled to -196° and hexafluoropropene oxide (16.6 g., 0.10 mole) was condensed into the tube which was again shaken at room temperature (72 hrs). The tube was cooled in ice and methanol (ca. 15 ml.) was taken into the tube which was shaken for 1 hr. The reaction mixture was poured into ice/water and the organic products were extracted with ether, the extract was dried ( $\text{CaSO}_4$ ) and the ether was removed by distillation. Fractional distillation of the remaining material yielded  $\text{CF}_3\text{CHFCO}_2\text{Me}$  (3.2 g.) and a higher boiling fraction which is at present under

Reaction of Cyanide ion and Hexafluoropropene Oxide.

Dry potassium cyanide (6.5 g., 0.10 mole) and dried dimethylformamide (ca. 35 ml) were placed in a Fisher-Porter tube. The tube was cooled to  $-196^{\circ}$  and evacuated, hexafluoropropene oxide (16.6 g., 0.10 mole) was condensed into the tube which was then shaken at  $30^{\circ}$  (48 hrs). After cooling to  $-78^{\circ}$ , methanol (ca, 15 ml.) was taken into the tube which was then shaken whilst attaining room temperature. The contents were poured into water and the organic material was extracted with ether, the ether extract was dried ( $\text{CaSO}_4$ ) and the ether removed by distillation. A viscous black tar remained which was not investigated further. A repeat of this reaction using diglyme as solvent also yielded a viscous tar.

The reaction of zinc cyanide and hexafluoropropene oxide.

Zinc cyanide (11.7 g., 0.10 mole) and dry diglyme (ca. 30 ml.) were placed in a Fisher-Porter tube which was evacuated and cooled to  $-196^{\circ}$ . Hexafluoropropene oxide (16.6 g., 0.10 mole) was condensed into the tube which was then shaken at room temperature (ca.  $28^{\circ}$ ) for 220 hrs. The tube was cooled in dry ice/acetone and methanol (20 ml.) was added. The tube was shaken whilst attaining ambient temperature. The contents of the tube were poured into water, the solid material was filtered off and washed with ether. The filtrate was extracted with ether then washed with water and dried ( $\text{CaSO}_4$ ). The ether was removed by distillation and the remaining material (14.0 g) was separated by preparative g.l.c. into 2 components. Identification of these compounds could not be definitely made.

The reaction of  $\text{CF}_3\text{CFCF}_2$  and Ag CN.

A Fisher-Porter tube was loaded with dried AgCN (13.4 g., 0.10 mole), calcium oxide (5.6 g., 0.10 mole) and acetonitrile

(35 ml.). The tube was cooled to  $-196^{\circ}$ , evacuated, and hexafluoropropene oxide (16.6 g., 0.10 mole) was condensed in. The tube was shaken at ca  $28^{\circ}$  (240 hours), then cooled to  $-78^{\circ}$  and methanol (20 ml) added and again shaken whilst attaining room temperature (1 hour) then for a further 2 hours. The volatile contents of the tube were vented into an external trap at  $-78^{\circ}$  (unreacted  $\text{CF}_3\text{CF}(\text{O})\text{CF}_2$ ).

The remaining material in the tube was poured into ice-water and extracted with ether. The ether extract was dried ( $\text{CaSO}_4$ ) and the ether was removed by distillation to leave a material (2.4 g), g.l.c. analysis of which indicated a mixture of eight components.

#### Reaction of calcium carbide and hexafluoropropene oxide.

Calcium carbide (6.4 g., 0.10 mole) and acetonitrile (ca. 60 ml.) were placed in an autoclave which was sealed, cooled to  $-196^{\circ}$  and evacuated. Hexafluoropropene oxide (33.2 g., 0.20 mole) was condensed into the autoclave which was then rocked at  $80-90^{\circ}$  (36 hr.). The autoclave was cooled in dry ice/acetone and methanol (30 ml.) added, then rocked whilst attaining room temperature. The contents of the autoclave were then filtered and the filtrate poured into water. The organic material was extracted with ether, the extract was washed with water (6x 200 ml.) then dried ( $\text{CaSO}_4$ ). After removal of ether, a small amount of tarry material was obtained.

The reaction was repeated using sulpholane, in this case  $\text{CF}_3\text{CF}_2\text{CO}_2\text{Me}$  (50% yield) was the only isolated product. When carried out in diglyme or tetraglyme, the ester  $\text{CF}_3\text{CF}(\text{OMe})\text{CO}_2\text{Me}$  was obtained (ca. 50%). A tar was obtained when the reaction was carried out using benzonitrile as solvent.



Attempted reaction of lithium acetylide and hexafluoropropene oxide

The ethylene diamine complex of lithium acetylide,  $\text{LiC}\equiv\text{CH} \cdot \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (9.2 g., 0.10 mole) and diglyme (40 ml) were placed in 120 ml capacity steel autoclave. The autoclave was evacuated, cooled to  $-196^\circ$  and hexafluoropropene oxide (16.6 g., 0.10 mole) was condensed. The autoclave was rocked at  $28^\circ$  (24 hrs.). After reacting the volatile products were vented into a trap cooled to  $-78^\circ$  (hexafluoropropene oxide and acetylene) and the remaining reaction mixture was poured into ice/conc. HCl, again products were extracted with ether. The ether extract was washed with water, dried ( $\text{CaSO}_4$ ) and the ether was removed by distillation to yield ca. 1.0 g of tarry material which was not investigated further.

The preparation of  $\text{HC}\equiv\text{CNa}$  and reaction with hexafluoropropene oxide

Sodium metal (4.6g., 0.20g. atom) was placed in a flask with dry toluene (80 ml.). The flask was heated until the Sodium melted, the flask was stoppered, shaken vigorously, then cooled rapidly. The toluene was siphoned off the finely divided sodium, which was then washed with THF(2x100 ml.). Dry THF (freshly distilled from  $\text{LiAlH}_4$ ) was placed in the flask and acetylene gas was bubbled in. (Acetone was removed from the acetylene by passage through 2 dry ice/acetone traps) The solution became cloudy and the temperature rose to  $50^\circ$ . The reaction mixture was then heated to  $55^\circ$  (1 hr.) to ensure complete reaction. The flask was cooled to  $-10^\circ$  and hexamethyl phosphorous triamide (10 ml.) was added. Hexafluoropropene oxide was bubbled into the reaction mixture slowly, the mixture blackened immediately and after the addition of approx. 2g. of epoxide an explosion occurred.

The reaction was repeated using identical conditions except hexamethyl

phosphorous triamide was not added to the reaction mixture and hexafluoropropene oxide (33.2g., 0.20 mole) was added via a dry ice/acetone condenser. The reaction mixture again blackened, it was poured onto ice/HCl and the organic material extracted with ether, the ether extract was washed with water then dried ( $\text{CaSO}_4$ ). Removal of ether by distillation yielded only a viscous tar.

#### Preparation of iodine monochloride.

Iodine (1530 g., 6.0 g. atoms) was placed in a flask fitted with a gas inlet tube and reflux condenser. Chlorine gas was passed into the flask until the contents became completely liquid. The iodine monochloride was reacted directly with chlorotrifluoroethylene.

#### Reaction of iodine monochloride and chlorotrifluoroethylene.

A 1200 ml. autoclave was loaded with iodine monochloride (863 g., 5.3 g. atoms) and chlorotrifluoroethylene (600 g., 5.2 moles). The autoclave was rocked at  $26^\circ$  (55 hrs), then opened and the contents washed with 10% aqueous sodium bisulphite, water, and dried ( $\text{MgSO}_4$ ). Fraction distillation using a Vigreux column and partial take-off head afforded  $\text{CF}_2\text{ClCFClI}$  (1130 g., 4.1 moles, 78%).

#### Preparation of $\text{CF}_2\text{ClCFClCFClCF}_2\text{Cl}$

A 2000 ml flask fitted with a mechanical stirrer, reflux condenser and addition funnel was loaded with  $\text{CF}_2\text{ClCFClI}$  (700 g., 2.5 moles), acetic anhydride (220 ml) and dichloromethane (220 ml). Zinc dust (200 g.) was added to the contents of the flask in small amounts over 5 hours. The reaction mixture was stirred at room temperature overnight, the unreacted zinc was removed by filtration and dilute sulphuric acid added dropwise to hydrolyze acetic

anhydride present. The organic layer was washed with water (4 x 800 ml), then neutralized with saturated potassium carbonate solution and washed again with water, then dried ( $\text{CaSO}_4$ ). After removal of dichloromethane, fractional distillation of the remaining material yielded  $\text{CF}_2\text{ClCFClCFClCF}_2\text{Cl}$  (182 g., 0.60 mole, 48%) b.p. 133-138°.

Dechlorination of  $\text{CF}_2\text{ClCFClCFClCF}_2\text{Cl}$ .

Zinc dust (325 g., 5.0 g. atoms) and ethanol (600 ml) were placed in a flask which was fitted with a mechanical stirrer, addition funnel and reflux condenser the top of which was connected, via rubber tubing, to a -78° cold trap. The reaction mixture was heated to reflux with rapid stirring and  $\text{CF}_2\text{ClCFClCFClCF}_2\text{Cl}$  (180.0 g., 0.59 mole) was added slowly (4 hr.). The gas collected in the cold trap was passed through 10% aqueous sodium hydroxide, the fractionally condensed in vacuo to yield perfluorobutadiene (89.0 g., 0.55 mole, 93%) which was characterized by i.r. spectroscopy.

Preparation of Perfluorobutyryl fluoride.

Potassium fluoride used in this reaction was dried by heating to 150-160° in vacuo (2 days). Diglyme used was distilled from lithium aluminium hydride.

Potassium fluoride (75.0 g.) and diglyme (250 ml) were heated in a 1000 ml flask to 120° with rapid stirring. Perfluorobutyryl chloride (100.0 g., 0.46 mole) was added slowly (4 hr.). The perfluorobutyryl fluoride formed was distilled from the reaction mixture via a Vigueux column and partial take-off head. The distillate was then subjected to careful fractional distillation, perfluorobutyryl fluoride (82.5 g., 0.38 mole, 83%) was obtained, b.p. 12-14°, which was characterized by ir spectroscopy.

### Preparation of perfluoroglutaryl fluoride

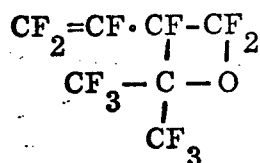
Potassium fluoride and diglyme used in this reaction were dried as described in the previous experiment.

Potassium fluoride (128.0 g., 2.2 moles) and diglyme (480 ml) were placed in a flask fitted with a mechanical stirrer, addition funnel and Vigreux column surrmounted by a partial take-off head. The reaction mixture was heated to 125° and stirred rapidly while perfluoroglutaryl chloride (200 g., 0.73 mole) was added. Crude perfluoroglutaryl fluoride was distilled from the reaction mixture continuously, then carefully fractionated to yield the pure compound (158.0 g., 0.65 mole, 90%) b.p. 46-47°, which was characterized by i.r. spectroscopy.

### Reaction of hexafluoroacetone and perfluorobu tadiene

Hexafluoroacetone (9.95 b., 0.06 mole) and perfluorobutadiene (10.0 g., 0.06 mole) were placed in a ultraviolet reactor (Hanovia 450 watt lamp) and irradiated (10 hr.).

After reaction the non volatile material was distilled to yield a major component b.p. 71-76°, which has been tentatively identified by i.r. and n.m.r. spectroscopy as



### Reaction of $\text{CF}_2=\text{CFCF}=\text{CF}_2$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{COF}$

$\text{CF}_3\text{CF}_2\text{CF}_2\text{COF}$  (30.2 g., 0.14 mole) and  $\text{CF}_2=\text{CFCFCF}_2$ , (11.3 g., 0.08 mole) were condensed into a ultra-violet reactor and then irradiated with a 450 watt Hanovia lamp (12 1/2 hrs.). The reaction mixture was removed from the reactor and fractionally distilled to yield a single component bp 59° and a residue which was shown by glc to be a complex mixture. Further investigation /

of the comparent b.p.  $59^{\circ}$  indicated it to be perfluoro-n-hexane (this was characterized by comparison of nmr and infrared spectra with those of a known pure sample sample).

#### Reaction of Lithium Chloride and Hexafluoropropene oxide

Anhydrous lithium chloride (8.5 g., 0.20 mole) and diglyme (50 ml, distilled from  $\text{LiAlH}_4$ ) were placed in a Fisher-Porter tube. The tube was cooled to  $-196^{\circ}$  and evacuated, hexafluoropropene oxide (33.2 g., 0.20 mole) was condensed in. The tube was shaken at room temperature (24 hrs). Then methanol (20 ml) was added. The tube was opened, and the contents poured into water, the organic material was extracted with ether. The ether extract was dried and ether removed by rapid distillation. Fractional distillation of the remaining material yielded methyl  $\alpha$ -chloro-perfluoropropionate (35.8 g., 0.184 mole, 92%) identified by nmr spectroscopy.

#### The reaction of hexafluoropropene oxide and perfluoroglutaryl fluoride

Diglyme was diatilled from lithium aluminium hydride immediately before use.

A 1 litre 3-neck flask was fitted with an addition funnel, magnetic stirrer, thermometer and rubber septum. Caesium fluoride (7.6 g., 0.05 mole) was placed in the flask and heated at  $170^{\circ}$  (18 hr) at full vacuum. The flask was cooled and let down to dry nitrogen. Diglyme (72 ml) and perfluoroglutaryl fluoride (122.0 g., 0.50 mole) were placed in the flask whilst purging with dry nitrogen. The flask was closed and exacuated to 90 mm Hg and hexafluoropropene oxide was bubbled into the flask through a sintered tube.

After the addition of 690 g of hexafluoropropene oxide a

ml of the reaction mixture was analyzed by glc, this showed

the prescence of mainly hexafluoropropene oxide tetramer, pentamer and hexamer in addition to 5 and 6 EDAF's. The reaction was continued until a total of 1120 g. of hexafluoropropene oxide had been added. At this point glc analysis of the reaction mixture indicated the following approximate composition.

(HFPO) <sub>3</sub>	7.5%	6-EDAF	4%
(HFPO) <sub>4</sub>	7%	7-EDAF	25%
(HFPO) <sub>5</sub>	24%	8-EDAF	15%
(HFPO) <sub>6</sub> or 4EDAF	15%	9-EDAF	trace
5-EDAF	1.5%		

The upper diglyme layer was separated from the acid fluoride layer and the acid fluoride mixture was placed in a 1 litre distilling flask with a thermometer-well. Extremely careful fractional distillation of this material was carried out using a silvered vacuum-jacketed column (2 1/2 feet) packed with glass helices (1/4" dia) and a partial take-off head. Below are listed the major fractions obtained, intermediate fractions are not listed.

Boiling range	pressure, mm. Hg	weight, g.	composition
30-35	0.25-0.30	117	(HFPO) <sub>4</sub> 95%
40-45	0.25	96	(HFPO) <sub>5</sub> 98%+
46-60	0.25	65	(HFPO) <sub>6</sub> or 4-EDAF 83%
63-78	0.20	20	5-EDAF 80%; 6EDAF 20%
78-80	0.10	78	6-EDAF 90%; 7-EDAF 10%
103-107	0.10-0.08	345	7-EDAF 93%; 8-EDAF 85%
118-119	0.08	127	8-EDAF 95%; 9-EDAF 5%
120-123	0.08	31	8EDAF 13%; 9-EDAF 87%

### Preparation of the dipotassium salt of EDAF (5-7)

EDAF (5-7)(78.0g.) were added to water (250 ml) with rapid stirring (2hr.). Potassium carbonate solution (10%) was added until the solution became neutral to litmus. Benzene was added to the mixture and the water was removed by azeotrope formation with benzene. Considerable difficulty was encountered during this operation due to foaming of the reaction mixture. After removal of water and benzene the fine white powder was dried in vacuo over phosphorous pentoxide (6 days).

### Pyrolysis of the dipotassium salts of EDAF (5-7).

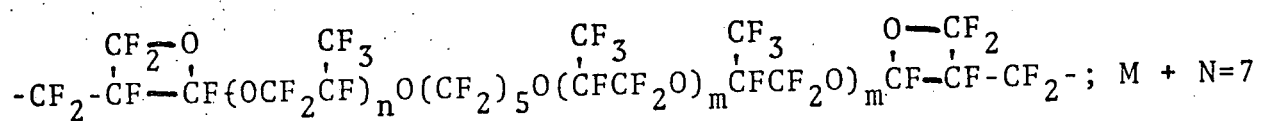
The dipotassium salt (ca. 50.0g.) was weighed out in a dry-box and placed in a pyrex glass ampoule (ca. 150 ml. capacity). The tube was heated within furnace at  $230-240^{\circ}$  (14 days) whilst connected to an external trap cooled in liquid nitrogen, the whole apparatus being evacuated (0.10mm Hg.). The reaction yielded 30.2g. of a colourless liquid which was shown by i.r. spectroscopy to contain the  $\text{CF}_2=\text{CF}$ - grouping.

### Photolysis of perfluoro-1,5-hexadiene and 7,8-EDAF

A. 7-EDAF (25.0 g.) were placed in a silica glass ampoule (approx. capacity 150 ml.), and held at full vacuum (1 hr.) to remove dissolved gases. The tube was cooled to  $-196^{\circ}$  and perfluoro-1,5-hexadiene (1.0 g.) was condensed into the tube. The tube was sealed in vacuo then warmed to room temperature and irradiated at a distance of ca. 20 mm from a 450 watt Hanovia ultraviolet source (130 hrs.).

After reaction viscous liquid material was poured from the tube, the remaining semi-solid material was refluxed with Freon 113 (2 lv.). Material insoluble in Freon 113 was separated, washed with Freon 113 then dried in vacuo. Microanalysis of this material (165-E):

Found: C, 22.41; H, 0.03; F, 68.22 calculated for the repeating unit,



C, 23.0; H, 0 ; F, 68.3%.

(End groups disregarded; characteristics of material indicated acyl fluoride end groups.)

Material soluble in Freon 113 was also separated as a semi-solid mass after removal of Freon 113.

B. Whilst purging with dried nitrogen 7,8-EDAF's (48.5 g.) and perfluoro-1,5-hexadiene (2.5 g.) were placed in a ultraviolet reactor consisting of an outer vessel and an inner water cooled quartz glass lamp tube. The vessel was placed in a horizontal position and the material in the outer jacket was irradiated (165 hrs). During irradiation (450 watt Hanovia lamp) solid material became apparent in the reaction mixture, especially at the liquid/glass interfaces. After reaction a viscous liquid material (199-A) was poured from the vessel. The remaining material was washed from the vessel with Freon 113, and material insoluble in Freon 113 was separated (199-B). This insoluble material was refluxed with Freon 113 (3 hr.) and insoluble



material was separated, washed and all Freon 113 was removed (199-D)., (23.0 g). Infrared spectroscopy of material 199-A indicated the presence of acyl fluoride groups, also materials 199-B, 199-C, and 199-D appeared to contain acyl fluoride end groups.

Photolysis of perfluoro-1,5-hexadiene and 7,8-EDAF's followed by end-capping of material

7,8-EDAF's (32.5 g.,) and perfluoro-1,5-hexadiene (2.0 g.) were placed in a silica glass ampoule to which had been fitted a graded glass section and pyrex Fisher-Porter stopcock. The material in the tube was degased, then irradiated (72 hrs.) using a Hanovia 450 watt ultraviolet source. During this initial irradiation period solid material became apparent in the tube. The volatile material was pumped off (small amount of  $\text{COF}_2$  + CO) the tube cooled to  $-196^\circ$  and hexafluoropropene (ca. 1.0 g) was condensed into the tube. Irradiation was then carried out (12 hrs). Volatile material was again pumped from the tube (unreacted hexafluoropropene), the tube was cooled to  $-196^\circ$  and hexafluoroacetone (ca. 1.0 g.) was condensed into the tube. Irradiation was again carried out (12 hrs), and the volatile material (unreacted hexafluoroacetone) was pumped from the tube. The resultant material was washed from the tube. The resultant material was washed from the tube with Freon 113. Material which was insoluble in refluxing Freon 113 was separated (9.5 g) (249-A), in addition material insoluble in cold Freon 113 (249-B) and material soluble in cold Freon 113 (viscous liquid 249-C) were separated.

Photolysis of perfluoro-1,3-butadiene and EDAF's

7-EDAF (35.0 g.) was placed in a silica glass ampoule (capacity approx. 150 ml), the tube was evacuated and cooled to  $-196^{\circ}$ . Perfluoro-1,3-butadiene (1.5 g.) was condensed into the tube which was then sealed in vacuo and irradiated using a 450 watt Hanovia ultraviolet source (96 hrs). During this period solid material became apparent in the tube. The viscous liquid material was then poured from the tube (149-A), the remaining solid and semi-solid material was washed from the tube with Freon 113. Material soluble in refluxing Freon 113 (149-B) and material insoluble in refluxing Freon 113 (149-B) and material insoluble in refluxing (3 hrs) Freon 113 (149-C) (4.0 g) were separated, and Freon 113 removed in vacuo. This reaction was not repeated using the water-cooled ultraviolet reactor described previously due to the low boiling point of perfluoro-1,3-butadiene ( $6^{\circ}$ ).

Photolysis of perfluorobuta-1,3-diene and EDAF's followed by end-capping of material.

7,8,9-EDAF's (20.0 g.) were placed in a silica glass ampoule fitted with a Fisher-Porter stopcock and held in vacuo for 1 hour to remove dissolved gases. The tube was then cooled to  $-196^{\circ}$  and perfluoro-1,3-butadiene (1.0 g) was condensed into the tube. After attaining room temperature the tube was irradiated at a distance of approx 5 mm. from a Hanovia 450 watt ultraviolet lamp. During this time the temperature of the tube was  $80-90^{\circ}$ . Irradiation was carried out for 60 hours; during which time solid material became apparent in the tube, especially at the liquid-glass interface. The volatile materials (small amount

of  $\text{COF}_2$  and  $\text{CO}$ ) were pumped from the tube which was then cooled to  $-196^\circ$  and hexafluoropropene (1.0 g.) was condensed into the tube. Irradiation was then carried out (12 hr). Volatile material was again pumped from the tube (unreacted hexafluoropropene) it was cooled to  $-196^\circ$  and hexafluoroacetone (1.0 g) condensed into the tube irradiation was again carried out (12 hrs). Volatile material (unreacted hexafluoroacetone) was pumped from the tube and the material washed out with Freon 113. This was separated into three parts 253-A, insoluble in refluxing Freon 113 (3 hrs) (12.5 g); 253-B, insoluble in cold Freon 113 (4.3 g) and 253-C, soluble in cold Freon 113 (3.5 g).

#### Photolysis of perfluoro-1,7-octadiene and EDAF's

A. 7-EDAF (30.0 g) was placed in a silica glass ampoule and held under vacuum (1 hr) to remove dissolved gases. The tube was then cooled to  $-196^\circ$  and perfluoro-1,7-octadiene (1.5 g.) was condensed into the tube, which was irradiated at a distance of 20 min from a Hanovia 450 watt ultraviolet source (165 hrs). Viscous liquid material was poured from the tube. Semi-solid and solid materials were washed from the tube with Freon 113, and refluxed with Freon 113 (3 hrs). Material insoluble in refluxing Freon 113 was separated and Freon 113 removed to yield 10.5 g solid material (161 A). Material soluble in refluxing Freon 113 was also separated (161-B).

B. 7,8-EDAF mixture (29.0 g.) and perfluoro-1,7-octadiene (1.8 g) were placed in a ultraviolet reactor under dry nitrogen. The ultraviolet reactor consisted of a outer pyrex jacket and an

inner quartz glass water cooled lamp tube. The reactor was placed in a horizontal position and the material was irradiated (20 days). At the end of this irradiation period only a small amount of semi-solid material was present. The material was washed from the reaction vessel with Freon 113. The small amount (ca. 0.5 g) of insoluble material was separated, and after removal of Freon 113, a viscous liquid material remained (179-A).

Photolysis of perfluoro-1,7-diene and EDAF's followed by end capping of material

7,8,9-EDAF mixture (20.0 g) was placed in a silica-glass reaction tube fitted with a Fischer-Porter stopcock. The material was held in vacuo (1 hr) to remove dissolved gases. Perfluoro-1,7-octadiene (1.0 g) was condensed into the tube at  $-196^{\circ}$ . The tube was warmed to room temperature and irradiated at a distance of 5 mm. from a 450 watt Hanovia ultraviolet source (68 hrs). During this irradiation period the material in the tube became extremely viscous. Volatile material was then removed from the tube under vacuum (small amounts of  $\text{COF}_2$  and  $\text{CO}$ ), the tube was cooled to  $-196^{\circ}$  and perfluoro-1-heptene (1.5 g) condensed into the tube. This material was then irradiated (12 hours). Volatile contents of the tube were again removed (unreacted perfluoro-1-heptene) and the tube cooled to  $-196^{\circ}$  and hexafluoroacetone (1.0 g) was condensed into the tube, irradiation was again carried out (12 hrs). Volatile material (unreacted hexafluoroacetone) and the material was washed from the tube with Freon 113. After removal of Freon 113 only an extremely viscous liquid material was obtained (255-A).

Photolysis of EDAF's in the presence of ditrifluorovinyl compounds derived from EDAF's

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7,8-EDAF mixture (21.0 g.) and ditrifluorovinyl compounds derived from EDAF's (20.0g.) were placed in a ultraviolet reactor under dry nitrogen and irradiated (168 hrs) using a 450 watt Hanovia ultraviolet source. During reaction solid material became apparent in the reaction vessel. After reaction, viscous liquid material was poured from the reaction vessel (215-c, 18.4 g); the infrared spectrum of this material indicated the presence of acyl fluoride end groups. The remaining material was washed from the reaction vessel with Freon 113 and separated to yield material 215-A, insoluble in refluxing Freon 113 (3 hr) (16.5) and material soluble in refluxing Freon 113. Properties of these materials indicated the presence of acyl fluoroide end groups.

In a separate experiment 7,8,9-EDAF mixture (22.0 g.) and the ditrifluorovinyl compounds derived from 7,8-EDAF (20.0 g) were placed in a silica glass tube fitted with a Fisher-Porter stopcock. The material was held in vacuo (1 hr) in order to remove dissolved gases. The tube was then irradiated, during which time an explosion occurred (after approx. 12 hrs). It is presumed that the explosion was due to a fault in the tube since pressure build-up sufficient to blow the tube is unlikely.

# Photolysis of hexafluoropropene oxide tetramer and hexafluoropropene

Hexafluoropropene oxide tetramers (25 g) was placed in a quartz glass ampoule fitted with a Fisher Porter stopcock. The tube was connected to a gas storage bulb, mercury manometer and vacuum line. Hexafluoropropene was allowed to enter the system. Irradiation was carried out (24 hrs) using a Hanovia 450 watt lamp. After reaction liquid material was removed from the tube, the infrared spectrum of this material did not show absorption due to the acyl fluoride linkage.

## Preparation of $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CF}_2\text{O})\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CO}_2\text{K}$

Hexafluoropropene oxide pentamer,  $(\text{HFPO})_5$  (30.0 g) was added to water (2 hrs) with rapid stirring. Potassium carbonate solution (10%) was added until the mixture was neutral to litmus. Most of the water was removed by freeze-drying technique and the last amounts of water were removed from the potassium salt by drying over phosphorous pentoxide at full vacuum.

## Pyrolysis of $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CF}_2\text{O})_3\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CO}_2\text{K}$

Pyrolysis of the potassium salt of hexafluoropropene oxide pentane (20.0 g) at  $230^\circ$  (6 days) yielded the corresponding tri-fluorovinyl compound  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CF}_2\text{O})_3\text{CF}=\text{CF}_2$  (12.0 g) which was purified by fractional distillation.

## Photolysis of $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CF}_2\text{O})_3\text{CF}=\text{CF}_2$ in presence of hexafluoroace

The compound  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{CF}}}\text{CF}_2\text{O})_3\text{CF}=\text{CF}_2$  (10.0 g) was placed in a quartz glass ampoule fitted with a Fisher-Porter stopcock and connected to a gas storage bulb, mercury manometer and vacuum line.

Hexafluoroacetone was placed in the system. Irradiation was carried out (28 hrs), using a Hanovia 450 watt ultraviolet lamp. Liquid material was removed from the reaction tube, the infrared spectrum of this material indicated the absence of the  $\text{CF}=\text{CF}_2$  group.

Reaction of hexafluoropropene oxide and the sodium salt of diethylmalonate

See July report: This reaction yielded a complex mixture of at least six components. (as shown by g.l.c.). Separation of these products was not carried out.

Reaction of hexafluoropropene oxide and excess n-butyllithium

Reaction of n-butyllithium (0.60 mole) and hexafluoropropene oxide (33.2 g., 0.20 mole) was carried out in hexane/ether using a 1.4 l. autoclave at 50-55° (24 hrs). After reaction no volatile material remained in the autoclave, the reaction mixture was poured onto ice/dil. HCl and the organic material was extracted, washed with water, then dried ( $\text{CaSO}_4$ ). Hexane and ether were removed by distillation. Fractional distillation of the remaining material yielded the carbinol  $\text{CF}_3\text{CF}(\text{C}_4\text{H}_9)\text{C}(\text{C}_4\text{H}_9)_2\text{OH}$  (33.6 g., 0.11 mole, 55%) b.p. 93-94° at 1.0 mm Hg.  $^1\text{H}$  nmr, OH (singlet) 7.34 $\tau$  and complex absorption assigned to n- $\text{C}_4\text{H}_9$  groups between 7.60 and 8.72 $\tau$ .  $^{19}\text{F}$  nmr (TFA ref.), doublet -6.3 ppm ( $\text{CF}_3$ , J 5.5 Hz) and 99.0 ppm (complex multiplet CF). Infrared and mass spectra and also microanalysis confirmed the proposed structure.